Influence of Dipolar Interaction on Magnetic Properties of Ultrafine Ferromagnetic Particles

Jesús García-Otero,[1] Markus Porto,[2,*] José Rivas,[1] and Armin Bunde[2]

[1]*Departamento de Física Aplicada, Universidade de Santiago de Compostela, Campus Universitario, 15706 Santiago de Compostela, Spain*

[2]*Institut für Theoretische Physik III, Justus-Liebig-Universität Giessen, Heinrich-Buff-Ring 16, 35392 Giessen, Germany*

We use Monte Carlo simulations to study the influence of dipolar interaction and polydispersity on the magnetic properties of single-domain ultrafine ferromagnetic particles. From the zero field cooling (ZFC)/field cooling (FC) simulations we observe that the blocking temperature T_B clearly increases with increasing strength of interaction, but it is almost not effected by a broadening of the distribution of particle sizes. While the dependence of the ZFC/FC curves on interaction and cooling rate are reminiscent of a spin glass transition at T_B, the relaxational behavior of the magnetic moments below T_B is not in accordance with the picture of cooperative freezing.

In recent years, single-domain ultrafine ferromagnetic particles have received considerable interest, both due to their important technological applications and their rich experimental behavior (see [1] for a recent review). While dilute systems are well understood [2–6], the experimental results for dense systems are a matter of controversy [1,7–21]. In dense systems, the mutual interactions between the magnetic particles play a dominant role, but, due to experimental difficulties, it is not clear what the main effects of the interactions are. This is even true for the most basic interaction here, the magnetic dipolar interaction. For example, it has not been clarified yet if an increase in the concentration of particles leads to an increase in the effective potential barriers between the easy directions (as suggested in [9]) or to a decrease (as suggested in [12]), with the corresponding consequences on related experimental quantities. It is also not clear if the spin glass behavior recently reported for dense samples of γ-Fe$_2$O$_3$ [14], ϵ-Fe$_3$N [19], and amorphous Fe$_{1-x}$C$_x$ [21] can be attributed to an interplay between anisotropy and dipolar interaction, as conjectured in [13].

In order to shed light on the role of the magnetic dipolar interaction, and in particular on its interplay with the anisotropy of the particles, we have performed extensive Monte Carlo (MC) simulations. We have concentrated on perhaps the most basic model for ultrafine ferromagnetic particles, which assumes coherent magnetization rotation within a particle and takes into account their anisotropy and the dipolar interaction between them. From our results for the zero field cooling (ZFC) and field cooling (FC) susceptibilities we can conclude that (i) the blocking temperature T_B (roughly defined as the temperature where the ZFC susceptibility is at its maximum) increases with increasing concentration of particles, and (ii) the Curie-Weiss temperature T_0 tends to larger negative values with increasing concentration. In combination with simulations of the relaxational behavior (iii) we find, even in dense systems, no evidence for a spin glass

transition close to T_B and/or for a spin glass phase at lower temperatures.

In the model we assume that every particle i consists of a single magnetic domain with all its atomic moments rotating coherently, resulting in a constant absolute value $|\vec{\mu}_i| = M_S V_i$ of its total magnetic moment $\vec{\mu}_i$. Here, V_i is the volume of particle i, and M_S is the saturation magnetization that is supposed to be independent of particle volume and temperature. The energy of each particle i is composed of three parts: anisotropy energy (either due to the shape or the crystalline structure of the particle), field energy, and interaction energy. For the sake of simplicity, we consider a temperature independent uniaxial anisotropy

$$E_A^{(i)} = -KV_i\left(\frac{\vec{\mu}_i \cdot \vec{n}_i}{|\vec{\mu}_i|}\right)^2, \qquad (1)$$

where K is the anisotropy constant and the unit vector $\vec{n}_i$ denotes the easy directions. As usual, the coupling with the applied field $\vec{H}$ is described by

$$E_H^{(i)} = -\vec{\mu}_i \cdot \vec{H}, \qquad (2)$$

and the magnetic dipolar interaction between two particles i and j separated by $\vec{r}_{ij}$ is given by

$$E_D^{(i,j)} = \frac{\vec{\mu}_i \cdot \vec{\mu}_j}{r_{ij}^3} - \frac{3(\vec{\mu}_i \cdot \vec{r}_{ij})(\vec{\mu}_j \cdot \vec{r}_{ij})}{r_{ij}^5}. \qquad (3)$$

Adding up Eqs. (1)–(3) and summing over all particles, we obtain the total energy

$$E = \sum_i E_A^{(i)} + \sum_i E_H^{(i)} + \frac{1}{2}\sum_i \sum_{j\neq i} E_D^{(i,j)}. \qquad (4)$$

In our numerical study, we have considered samples of $N = 64$ particles, with volumes V_i drawn from a normal distribution $P(V) \propto \exp\{-(V - \overline{V})^2/(2\sigma_V^2)\}$, with the mean volume $\overline{V}$ fixed and widths σ_V ranging from $\sigma_V = 0$ (δ distribution) to $\sigma_V = 0.3\overline{V}$. The unitless concentration c is defined as the ratio between the total volume $\sum_i V_i$ 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 $c = 0.32c_0$, where $c_0 \equiv 2K/M_S^2$ is a unitless material constant of the order of unity [22].

In order to achieve a liquidlike arrangement of the particles similar to a ferrofluid without aggregations, the particle positions were chosen from an inverse MC simulation procedure in which the particles move freely and interact by a standard Lennard-Jones pair potential [23] with periodic boundary conditions [24]; see Fig. 1 for the obtained pair correlation function $g_2(r)$ [25]. The easy axes of the particles were chosen randomly. In the subsequent MC simulation, both positions of the particles and their easy axes are kept fixed. For treating the long-range dipolar interaction without any truncations we applied periodic boundary conditions using Ewald's summation for an infinite sphere surrounded by vacuum [24,26].

For studying the time dependent magnetization during cooling and heating, we employed the standard Metropolis algorithm [27] with local dynamics (see also [28]): In every step, we select a particle i at random and generate an attempted orientation $\vec{\mu}_{att}^{(i)}$ of its magnetization, chosen in a spherical segment around the present orientation $\vec{\mu}^{(i)}$ with an aperture angle $\delta\theta$ [29]. The attempted orientation is accepted with probability $\min[1, \exp(-\Delta E/k_B T)]$, where ΔE is the energy difference between attempted and present orientation, and k_B is the Boltzmann constant. After each trial, the time is incremented by N^{-1}, so in one time unit (one Monte Carlo step) N attempts are made. The magnetization along the field is recorded in certain time intervals, and an ensemble average is performed by repeating the respective simulation for typically 300 samples with different realizations of spatial arrangements, orientations of the easy axes, and particle volumes (the latter for the cases where the size of each particle is not fixed but chosen randomly from a distribution).
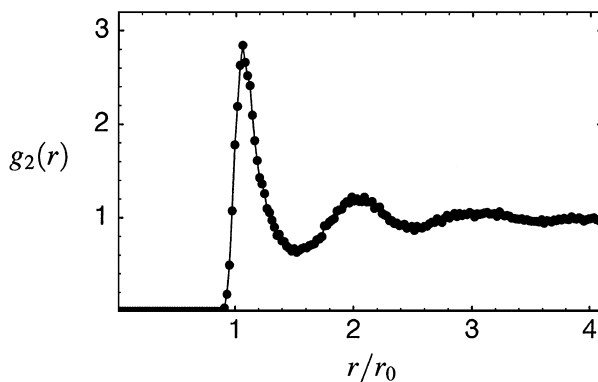
First we consider simulations of zero field cooling/field cooling experiments. In a ZFC experiment, the sample is first demagnetized at very high temperature and cooled down in zero field. Then, at very low temperature a small external field is applied and the sample is heated up at constant rate until well above the blocking temperature. In the subsequent FC experiment, the small field is maintained and the sample is cooled down again at the same constant rate. During the whole ZFC/FC experiment the magnetization M along the field is measured, from which the susceptibility χ follows. In a typical ZFC measurement the susceptibility χ_{ZFC} increases with increasing temperature until the blocking temperature T_B is reached. Above T_B, in the superparamagnetic regime, χ_{ZFC} decreases monotonically with increasing temperature. In the FC experiment the susceptibility χ_{FC} coincides with χ_{ZFC} until the blocking temperature is reached (since above T_B the system is able to reach thermal equilibrium within the time lag between the measurements), and tends to a constant value at low temperatures. The blocking temperature will depend on the heating rate, approaching zero at infinitely slow heating rate.

Our numerical results for the reduced susceptibilities are in agreement with this picture. We have determined $\chi \equiv (M/M_S)/(H/H_A)$ from ZFC/FC simulations, for an applied field $H = 0.1H_A$ and a constant temperature decrease/increase of $\Delta T = 0.0245K\overline{V}/k_B$ every 2000 Monte Carlo steps. Figure 2 shows the effect of polydispersity on the behavior of χ_{ZFC} and χ_{FC} for (a)
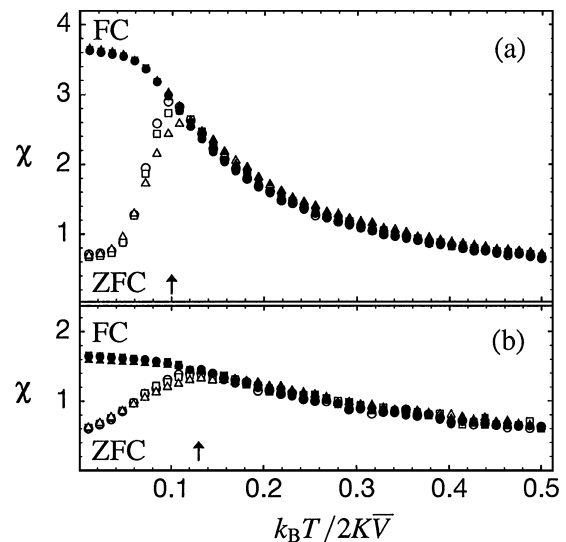

FIG. 2. Plot of the reduced susceptibilities χ_{ZFC} (open symbols) and χ_{FC} (full symbols) vs reduced temperature $k_B T/(2K\overline{V})$: (a) in the dilute limit and (b) for a concentration $c/c_0 = 0.128$ of particles, for size distribution with widths $\sigma_V/\overline{V} = 0$ (open and full circles), 0.15 (open and full squares), and 0.3 (open and full triangles). The arrows indicate the respective blocking temperatures T_B. In all figures the size of the symbols roughly corresponds to the error bars.

FIG. 1. Plot of the pair correlation function $g_2(r)$ vs r/r_0 of the liquidlike arrangements obtained by the inverse MC simulation technique. The parameter r_0 marks the beginning of the repulsive wall of the potential. For large distances, the particles are uncorrelated and $g_2(r) = 1$.

systems without dipolar interaction (corresponding to the dilute limit) and (b) for a dense system (concentration $c/c_0 = 0.128$). In both cases the curves do almost not depend on the distribution of particle sizes ($\sigma_V/\overline{V} = 0$, 0.15, and 0.3). Thus we can conclude that within the framework of the present model the dynamical behavior of ultrafine ferromagnetic particles is almost not affected by a moderately broad volume distribution. In the following, we restrict ourselves to a constant volume, where the influence of the dipolar interaction can be worked out most clearly.

In Fig. 3 we have plotted χ_{ZFC} and χ_{FC} for different particle concentrations, from the dilute limit to $c/c_0 = 0.32$. The figure reveals the effect of the dipolar interaction on the blocking temperature T_B: T_B increases with increasing concentration. In order to show the effect of the interaction on the Curie-Weiss temperature T_0, we have plotted, in the inset of Fig. 3, χ_{FC}^{-1} as a function of the reduced temperature $k_B T/(2K\overline{V})$. The figure shows that well above T_B, χ_{FC} indeed follows the Curie-Weiss law, $\chi_{FC} \propto (T - T_0)^{-1}$, with $T_0 = 0$ in the dilute limit. With increasing particle concentrations, T_0 becomes negative and its absolute value increases. This result agrees well with most experimental findings. In some experiments, however, a decrease of T_B with increasing particle concentrations has been reported (see [12], and references therein). Our simulations suggest that this interesting feature has a different origin than dipolar magnetic interaction or polydispersity.

In Fig. 4 we are concerned with the question of a possible spin glass phase below T_B. The inset of Fig. 4 shows the ZFC/FC susceptibilities for two different heating rates
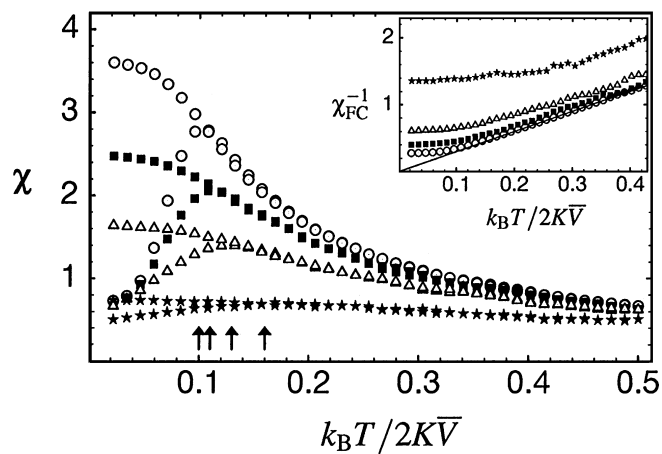
($\Delta T = 0.0245 K\overline{V}/k_B$ every 1000 and 8000 Monte Carlo steps respectively) for a particle concentration $c/c_0 = 0.128$. For the lower rate, T_B is shifted towards smaller values, as expected. Well above T_B the curves coincide while close to T_B the curves split, with larger values of the susceptibility for the slower process. This behavior together with the increase of T_B with increasing concentration (see Fig. 3) is reminiscent of a spin glass transition, and indeed, the existence of a spin glass transition in systems of ultrafine particles has been proposed in several recent articles [10,13,14,19,21]. In order to check if in our case T_B may be associated with a spin glass temperature, we have studied the relaxational behavior of the susceptibility well below T_B, for four different initial states (fully demagnetized sample, saturated sample, sample after the ZFC process, and sample after the FC process). As shown in Fig. 4 all susceptibilities relax towards the same point, which therefore can be regarded as the equilibrium point. This feature is not consistent with the assumption of a spin glass phase where cooperative freezing occurs. We like to note that in the absence of the anisotropy term, in a system of spatially disordered dipoles, the existence of a dipolar glass has been reported [30]. It is an interesting theoretical problem (but beyond the scope of this work) to find out if the present system can show or not, for very small finite anisotropies, a transition to a spin glass phase.
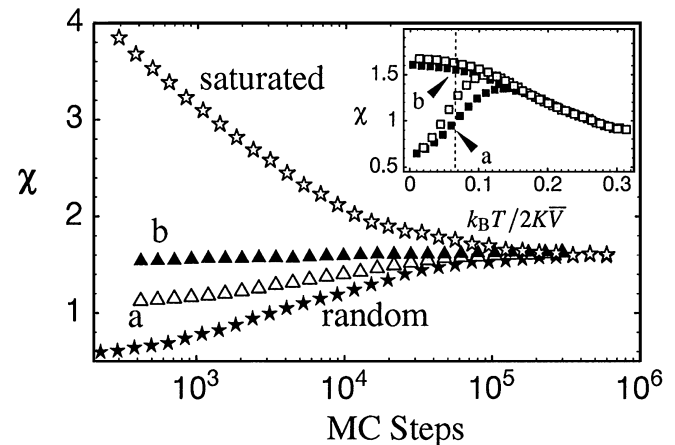

FIG. 4. Relaxational behavior of the reduced susceptibilities of a system of monodisperse interacting magnetic particles with concentration $c/c_0 = 0.128$ at a reduced temperature $k_B T/(2K\overline{V}) = 0.066$ well below the blocking temperature (the dashed line in the inset indicates this relaxation temperature). Shown are the relaxation of the susceptibility of (i) a fully saturated sample (open stars), (ii) a fully demagnetized sample (full stars), (iii) the system after a ZFC process (open triangles), and (iv) after a FC process (full triangles). These last two initial states are marked also in the inset as (a) and (b), respectively. All susceptibilities relax towards the same value, being larger than χ_{FC}. The inset shows the ZFC/FC curves for two different cooling rates: $\Delta T = 0.0245 K\overline{V}/k_B$ every (i) 1000 MC steps (full squares) and (ii) 8000 MC steps (open squares). The points (a) and (b) of the faster experiment were the ones chosen as initial states for relaxation shown in the main figure.

FIG. 3. Plot of the reduced susceptibilities χ_{ZFC} and χ_{FC} vs reduced temperature $k_B T/(2K\overline{V})$ for monodisperse magnetic particles in the dilute limit (open circles) as well as for concentrations $c/c_0 = 0.064$ (full squares), 0.128 (open triangles), and 0.32 (full stars). The arrows indicate the respective blocking temperatures T_B. The inset shows the inverse reduced FC susceptibility χ_{FC}^{-1} as a function of the reduced temperature $k_B T/(2K\overline{V})$ for the same parameters; the straight line has a slope of 3.

In summary, we have studied a simple model for ultrafine magnetic particles, which takes into account the most basic features of the system, anisotropy of the particles and dipolar interaction between them. We find that the model describes quite well the overall experimental situation, but we did not find evidence of a spin glass phase. We can conclude therefore that the interplay between anisotropy and magnetic interaction does not lead to a spin glass behavior. Other types of interaction that we did not consider here (e.g., exchange interactions caused by aggregation of the particles) might be candidates for obtaining frustrated configurations.

———————

*Present address: School of Chemistry, Tel Aviv University, 69978 Tel Aviv, Israel

[1] J. L. Dormann, D. Fiorani, and E. Tronc, Adv. Chem. Phys. **98**, 283 (1997).

[2] E. C. Stoner and E. P. Wohlfarth, Philos. Trans. R. Soc. London A **240**, 599 (1948); reprinted in IEEE Trans. Magn. **27**, 3475 (1991).

[3] L. Néel, Ann. Geophys. **5**, 99 (1949).

[4] W. F. Brown, Phys. Rev. **130**, 1677 (1963).

[5] A. Aharoni and I. Eisenstein, Phys. Rev. B **11**, 514 (1975).

[6] W. T. Coffey, D. S. F. Crothers, Y. P. Kalmykov, E. S. Massawe, and J. T. Waldron, Phys. Rev. E **49**, 1869 (1994).

[7] S. Shtrikman and E. P. Wohlfarth, Phys. Lett. A **85**, 467 (1981).

[8] R. W. Chantrell and E. P. Wohlfarth, J. Magn. Magn. Mater. **40**, 1 (1983).

[9] J. L. Dormann, L. Bessais, and D. Fiorani, J. Phys. C **21**, 2015 (1988).

[10] R. W. Chantrell, M. El-Hilo, and K. O'Grady, IEEE Trans. Magn. **27**, 3570 (1991).

[11] W. Luo, S. R. Nagel, T. F. Rosenbaum, and R. E. Rosensweig, Phys. Rev. Lett. **67**, 2721 (1991).

[12] S. Mørup and E. Tronc, Phys. Rev. Lett. **72**, 3278 (1994).

[13] S. Mørup, Europhys. Lett. **28**, 671 (1994).

[14] T. Jonsson, J. Mattsson, C. Djurberg, F. A. Khan, P. Nordblad, and P. Svedlindh, Phys. Rev. Lett. **75**, 4138 (1995).

[15] J. L. Dormann *et al.,* Phys. Rev. B **53**, 14 291 (1996); J. L. Dormann, L. Spinu, E. Tronc, J. P. Jolivet, F. Lucari, F. D'Orazio, and D. Fiorani, J. Magn. Magn. Mater. **183**, L255 (1998).

[16] M. F. Hansen, F. Bødker, S. Mørup, K. Lefmann, K. N. Clausen, and P.-A. Lindgård, Phys. Rev. Lett. **79**, 4910 (1997).

[17] C. Djurberg, P. Svedlindh, P. Nordblad, M. F. Hansen, F. Bødker, and S. Mørup, Phys. Rev. Lett. **79**, 5154 (1997).

[18] M. F. Hansen and S. Mørup, J. Magn. Magn. Mater. **184**, 262 (1998).

[19] H. Mamiya, I. Nakatani, and T. Furubayashi, Phys. Rev. Lett. **80**, 177 (1998).

[20] C. Johansson, M. Hanson, M. S. Pedersen, and S. Mørup, J. Magn. Magn. Mater. **173**, 5 (1997).

[21] T. Jonsson, P. Svedlindh, and M. F. Hansen, Phys. Rev. Lett. **81**, 3976 (1998).

[22] To give an estimate for the concentrations in real units: In iron-nitride nanoparticles we have $M_S = 1182$ emu/cm^3 and $K = 10^6$ erg/cm^3 [19], which yields $c_0 = 1.43$. Maghemite particles with a mean diameter around 7.5 nm reported in [14] show $M_S = 420$ emu/cm^3 and $K = 1.9 \times 10^5$ ergs/cm^3, which gives $c_0 = 2.15$. Accordingly, the largest concentration considered in this Letter corresponds to $c = 0.46$ for ion-nitride nanoparticles and $c = 0.69$ for maghemite particles.

[23] During this inverse MC simulation, the particles can move freely in a cubic box and interact only by a standard Lennard-Jones pair potential $v_{LJ}(r) = 4\varepsilon[(r_0/r)^{12} - (r_0/r)^6]$ with periodic boundary conditions. We choose $\varrho^\star = 0.85$ as reduced density, start with a very high temperature, and decrease it slowly until its final value $T^\star = 0.77$.

[24] M. P. Allen and D. J. Tildesley, *Computer Simulation of Liquids* (Clarendon Press, Oxford, 1987).

[25] The pair correlation function $g_2(r)$ is defined as $g_2(r) = (4\pi\varrho N r^2)^{-1} \sum_i \sum_{i \neq j} \delta(r - r_{ij})$, where N is the number of particles and ϱ is their density.

[26] S. W. de Leeuw, J. W. Perram, and E. R. Smith, Proc. R. Soc. London A **373**, 27 (1980).

[27] K. Binder and D. W. Heermann, *Monte Carlo Simulations in Statistical Physics,* Springer Series in Solid State Science Vol. 80 (Springer, Berlin, 1992), 2nd ed.

[28] J. García-Otero, M. Porto, J. Rivas, and A. Bunde, J. Appl. Phys. **85**, 2287 (1999).

[29] By varying the aperture angle $\delta\theta$, i.e., the maximal jump angle, it is possible to modify the rate of acceptance to optimize the simulation. As a compromise between simulations at low and high temperatures we choose $\delta\theta = 0.075$ for all simulations.

[30] G. Ayton, M. J. P. Gingras, and G. N. Patey, Phys. Rev. Lett. **75**, 2360 (1995); Phys. Rev. E **56**, 562 (1997); S. Ravichandran and B. Bagchi, Phys. Rev. Lett. **76**, 644 (1996); Phys. Rev. E **54**, 3693 (1996). For a classical review on orientational glasses, see U. T. Höchli, K. Knorr, and A. Loidl, Adv. Phys. **39**, 405 (1990).