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Competition between dipolar and exchange interparticle interactions in magnetic nanoparticle films

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Abstract

The concentration dependence of the remanence, the coercivity and the blocking temperature of a three-dimensional random assembly of ferromagnetic nanoparticles interacting via exchange and dipolar forces is studied by Monte Carlo simulations. We find that interactions always suppress the coercivity, while they have opposite effects on the remanence of the sample. The crossover from dipolar-coupled to exchange-coupled behavior occurs when the two types of interactions have comparable strengths. The blocking temperature is always enhanced due to interactions, except for the case that particles coalesce and the sample is above the percolation threshold.

Keywords: Magnetic nanoparticles; Hysteresis; Blocking temperature; Interparticle interactions; Monte Carlo simulation

The crucial role of interparticle interactions in determining the response of an assembly of magnetic nanoparticles to an externally applied field as well as the temperature dependence of the magnetic properties has been recognized long ago (for a review see, Ref. [1]). The characteristics of the hysteresis loop (remanence and coercivity) and the blocking temperature have been previously shown to vary with nanoparticle concentration in granular metals and frozen ferrofluids [1]. The experimental trend has been successfully reproduced by a model that includes interparticle dipolar interactions [2,3]. Measurements in granular metals close to percolation have indicated the presence of intergranular exchange interactions with ferromagnetic character [4]. A model study for weakly coupled grains appeared recently [5] that demonstrated the effect of interparticle interactions on the hysteresis characteristics and the moment correlation function. More recent magnetic measurements in cluster-assembled films grown by cluster-beam deposition [6] indicated the presence of strong-interparticle exchange.

In this work we investigate the role of interparticle exchange in modifying the concentration dependence of the hysteresis characteristics and the blocking temperature of a nanoparticle assembly. The whole range of exchange constants strengths is studied, thus modeling the transition from well separated to coalesced particles.

We consider N identical magnetic particles with a spherical shape and diameter d, located inside a cubic box of edge length Ld. Particles are placed at random on the nodes of an auxiliary lattice and thus overlap is avoided. The total energy of the

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assembly reads

$$E = g\sum_{i,j}\frac{(\hat{m}_i\cdot\hat{m}_j) - 3(\hat{m}_i\cdot\hat{r}_{ij})(\hat{m}_j\cdot\hat{r}_{ij})}{r_{ij}^3} - J\sum_{\langle i,j\rangle}(\hat{m}_i\cdot\hat{m}_j) - k\sum_i(\hat{m}_i\cdot\hat{e}_i)^2 - h\sum_i(\hat{m}_i\cdot\hat{H}). \qquad (1)$$

The ith particle carries a magnetic moment $\hat{m}_i$ and has uniaxial anisotropy ($k = K_1V$) along a random direction $\hat{e}_i$. The particles interact via long-range dipolar forces ($g = m^2/d^3$) and exchange forces (J). The latter act only between particles in contact (nearest neighbors). The dipolar energy is calculated for periodic boundaries and using the Ewald summation technique. Recent studies [7] of the ground state of interacting dipoles with finite size showed that the magnetic behavior is similar to that of point dipoles. These results justify the use of point dipoles in our model. The equilibrium spin configuration is obtained by a Monte Carlo simulation using the standard Metropolis algorithm [2]. Simulations are performed in a box with $L = 10$. For every field and temperature values the first 10^3 Monte Carlo steps per spin are used for thermalization and the subsequent 10^4 steps are used to obtain thermal averages. Averages over 10–30 particle configurations are taken in all cases. We choose here parameters that correspond to Fe nanoparticles [6], namely, the mean particle diameter $D = 3.0\,\mathrm{nm}$, the saturation magnetization $M_s = 1.7\times10^6\,\mathrm{A/m}$ and the anisotropy energy density $K_1 = 2.4\times10^5\,\mathrm{J/m^3}$, which provide $g/k = 0.65$. The value of the exchange energy (J) cannot be extracted from measurements in dilute samples in a straightforward manner and we therefore treat it here as a free parameter.

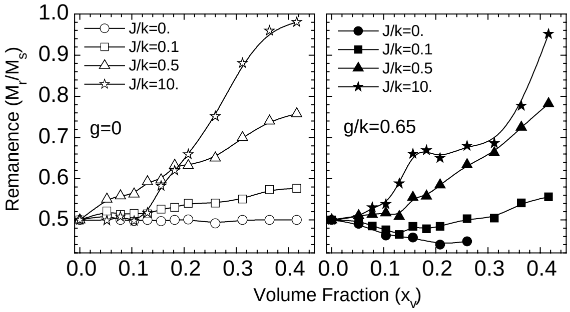

Fig. 1. Concentration dependence of remanence at low temperature ($t/k = 0.01$). Left panel: exchange coupling only ($g = 0$). Right panel: exchange and dipolar coupling ($g/k = 0.65$).

Results for the remanence at low temperature ($t/k = 0.01$), which is well below the blocking of the isolated nanoparticles ($t_b/k = 0.13$), are shown in Fig. 1. In the extreme dilute limit the theoretically predicted value of $M_r/M_s = 0.5$ is obtained independently of the interaction strength and it remains independent of concentration for a non-interacting system (open circles). The effect of weak exchange forces (open squares and triangles) is to enhance the remanence, because they favor ferromagnetic alignment of the moments. Strong exchange forces (open stars) correspond to a system where particles coalesce and form magnetically coherent clusters. We assume that the directions of the individual easy axes are preserved after coalescence, therefore the resulting coherent clusters have weaker anisotropy than individual particles and this explains the initially weak dependence of M_r on concentration below the percolation limit ($x_c = 0.15$). Above the percolation limit a bulk ferrromagnet with saturated magnetization gradually forms, which explains the steep increase of the remanence. Dipolar forces on the other hand (closed circles) produce a suppression of the remanence with concentration, as found previously [2]. Thus dipolar and exchange forces compete in producing a trend for the concentration dependence of the remanence. When they have comparable strength (closed triangles) the system exhibits an approximately concentration-independent remanence below the percolation. The value $g/k\sim1$ defines the crossover from a dipolar-coupled to an exchange-coupled assembly. When particle coalescence occurs ($J/k = 10.0$), the formation of a large clusters right above the percolation threshold ($x = 0.15-0.35$) is accompanied by the generation of strong random dipolar fields in the sample that have a demagnetizing character [2]. The strong competition with the exchange forces in this regime leads to the weak concentration dependence of the remanence in this concentration

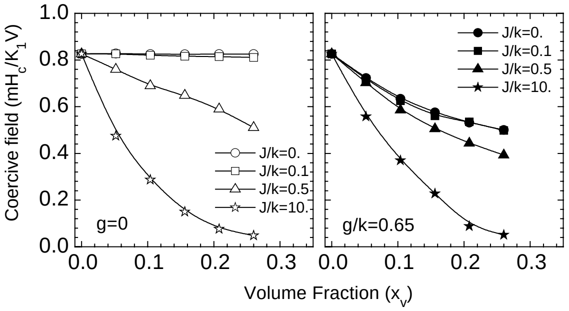

Fig. 2. Concentration dependence of coercivity at low temperature ($t/k = 0.01$). Left panel: exchange coupling only ($g = 0$). Right panel: exchange and dipolar coupling ($g/k = 0.65$).

region. Finally, in the dense limit ($x > 0.3$) exchange forces dominate and produce the bulk ferromagnetic behavior.

The concentration dependence of the coercivity is shown in Fig. 2. In the dilute limit the coercivity at zero temperature is theoretically predicted to approach the value of $H_c = 0.96K_1/M_s$. The data in Fig. 2 are slightly below this value due to the finite temperature ($t/k = 0.01$) at which the simulation is performed. Beyond the dilute limit, the effect of either type of interactions on the coercivity is quite similar, as the overall decrease of the coercivity values indicate. In the case of dipolar interaction only (closed circles) the reduction of coercivity is due to the demagnetizing character of the dipolar forces that is also responsible for the reduction of the remanence (see Fig. 1). On the other hand, exchange interactions favor the formation of ferromagnetic clusters of particles with low anisotropy, as explained earlier, and therefore the magnetization reversal is facilitated and the coercivity is reduced relative to the non-interacting case. When both types of interactions are present, we observe that their effect on the coercivity is not additive in all cases. In particular for weak exchange coupling (closed squares and triangles) the interactions act cooperatively and the coercivity is further reduced relative to the case of exclusively dipolar or exchange forces. However, in the case of particle coalescence (open stars) the introduction of dipolar forces in the sample of coalesced particles (closed stars) shifts the coercivity upwards. We attribute this behavior to the strong random dipolar fields generated in the sample containing large, almost isotropic, coherent clusters of particles. In this case, dipolar forces introduce an extra, albeit weak, anisotropy in the system that enhances the coercive field values.

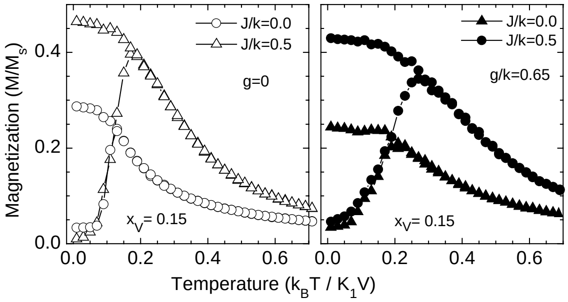

Fig. 3. Temperature dependence of magnetization (ZFC/FC curves). Left panel: exchange coupling only ($g = 0$). Right panel: exchange and dipolar coupling ($g/k = 0.65$). Applied field $h/k = 0.1$.

We discuss next the temperature dependence of the magnetization. The zero-field-cooled/field-cooled (ZFC/FC) curves are calculated and representative results for the case of weak exchange coupling are shown in Fig. 3. The peak of the ZFC curve provides the blocking temperature (T_b) of the system [1,8]. Interparticle interactions cause an increase of T_b and they modify the high temperature (superparamagnetic) behavior of the magnetization. In particular, Curie's law ($\chi \sim 1/T$) that is valid in the case of non-interacting superparamagnetic particles (open circles), is no longer obeyed by the interacting system. The deviations from Curie's law are stronger when both types of interactions are present (closed circles). In this case an almost linear decay with temperature is observed. Comparing the effect of the two types of interactions in the high temperature regime, we notice that dipolar interactions produce stronger deviations from Curie's law than exchange interactions and this is attributed to their long-range character. Consider, finally the dependence of the blocking temperature on concentration, as shown in Fig. 4. The general trend is that interparticle interactions enhance T_b relative to the non-interacting system and furthermore, that T_b increases with concentration. An interesting

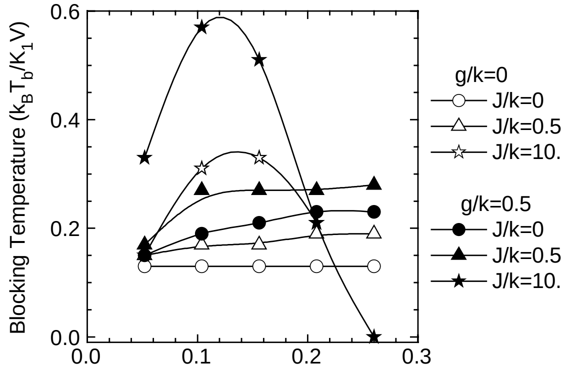

Fig. 4. Concentration dependence of blocking temperature.

observation that can be made from the data in Fig. 4 is that the contributions of the two types of interactions in the enhancement of T_b is not always additive. In particular, if we denote by $\Delta T_b(g)$ and $\Delta T_b(J)$ the increase of T_b relative to the non-interacting system when only dipolar (g) or exchange (J) interactions are present, respectively, then in the case of weak exchange (triangles) the total upshift of T_b when both interactions are present satisfies $\Delta T_b \approx \Delta T_b(g) + \Delta T_b(J)$. In other words, if we translate the upshift of T_b with an increase of the mean energy barrier for magnetization relaxation, the above relation implies that the two types of interactions produce additive contributions to the increase of the mean energy barrier. However, the situation is quantitatively different in the case of particle coalescence or strong exchange (stars). In this case and for concentrations below the percolation threshold ($x < 0.15$) the presence of both exchange and dipolar interactions produces a much bigger upshift of the blocking temperature than each type of interaction when it acts alone. The interpretation of this effect lies in the fact that the strong exchange changes the morphology of the system by creating coherent clusters of particles. The strong dipolar fields of these particles introduce an extra anisotropy in the system and lead to an increase of T_b. Qualitatively, this interpretation is the same as in the case of dipolar interactions only [1–3], the only difference is the strength of the dipolar fields which is much higher due to cluster formation. Above the percolation threshold ($x > 0.15$) an infinite coherent cluster forms with very weak anisotropy, which is the outcome of the coexistence of many local easy axes directions originating from the individual particles. The low anisotropy of the infinite cluster determines the blocking temperature of the system which is consequently very low.

In conclusion, we have studied the magnetic properties of a three-dimensional random assembly of interacting nanoparticles coupled via exchange and dipolar forces. We have shown that the coercivity decreases with concentration for all values of the exchange strength. The concentration dependence of the remanence is determined by the competition between the two types of interactions and the crossover them occurs when the strengths are comparable ($J \sim g$). The blocking temperature increases with concentration, except when particle coalescence occurs and the system is above the percolation limit.

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