Magnetic properties of dipolar interacting single-domain particles

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The remanence and coercivity of an assembly of single-domain ferromagnetic particles are studied using the Monte Carlo simulation technique. The particles have random locations, possess random uniaxial anisotropy, and are coupled through dipolar interactions. The dependence of the magnetic properties on the packing density, the size of the particles, and the temperature are examined systematically. The role of the packing geometry (sc, fcc) and the sample boundaries are discussed. Dipolar interactions are shown to reduce the coercivity with respect to values for the noninteracting assembly in all cases except for strongly dipolar systems below the percolation threshold. An enhancement of the remanence is found in weakly dipolar systems and is attributed to the macroscopic Lorentz field. The fcc packing of the particles leads to more pronounced ferromagnetic behavior than the sc packing. The sample free boundaries and the corresponding demagnetizing field have a strong effect on the remanence of the assembly while they produce a minor reduction to the coercivity. The results from the simulations are compared with magnetic measurements on frozen ferrofluids and granular metal solids. [S0163-1829(98)03241-X]

I. INTRODUCTION

The magnetic properties of small ferromagnetic particles with diameters typically about 10 nm are governed by two characteristic features. Namely, the single-domain magnetic structure and the enhanced coercivity. The former occurs because the size of the system is smaller than the exchange correlation length and the latter is a consequence of the reduced crystal symmetry near the surface originating from the finite size and possible existence of surface disorder.[1] As first pointed out by Néel in 1949, single-domain ferromagnetic particles exhibit the phenomenon of superparamagnetism. Namely, the reversal of their magnetization through a thermally activated process over the anisotropy barrier, even in the absence of an externally applied field. In other words, above a certain temperature (blocking temperature T_B) the ensemble of single-domain particles behaves as gas of paramagnetic molecules with giant magnetic moment ($m \sim 10^3 \mu_B$). The exploitation of this phenomenon in the determination of the particle size distribution has been the subject of intensive experimental and theoretical work over the last few years.[1,2]

Assemblies of small magnetic particles are formed by nature in many biological and geological systems (human blood, soils, rocks) or are prepared artificially. A strong motive for developing these systems is the basic understanding of their magnetic properties (finite size effects) as well as their unique technological applications.[2]

Among the most common artificially prepared systems containing fine magnetic particles are granular metal solids[3–5] that consist of fine magnetic particles (typically Fe, Ni, Co) embedded in a nonmagnetic matrix (typically SiO_2, BN, Al_2O_3, Cu, etc.). The technological importance of these systems arise from the fact that the preparation method allows tailoring of the magnetic properties of the system through a controlled variation of the average particle size and the metal volume fraction (x_v). Technological requirements for high packing densities make the role of interparticle interactions increasingly important,[1,6] as they modify significantly the magnetic properties of the assembly. These interactions can have a dipolar, Ruderman-Kittel-Kasuya-Yosida (RKKY), or a superexchange character, depending on the magnetic character of the matrix. For an insulating matrix, the dipolar interactions are the dominant ones. Major theoretical and experimental effort has been focused recently on the understanding of the role of the dipolar interactions in fine particle systems.[1] In addition to granular metal solids, frozen ferrofluids have been used to investigate the role of dipolar interactions. In these systems, the magnetic particles (usually Fe_3O_4, γ-Fe_2O_3) are held fixed in a frozen insulating liquid. The degree of dilution in the liquid solvent controls the average particle distance and therefore the strength of the interactions.[6–12]

The magnetic behavior of an assembly of noninteracting fine particles with uniaxial anisotropy is understood on the basis of Néel's arguments[13] that led to the concept of superparamagnetism.[14] For such an assembly, the coercive field decays with the square root of the temperature and for fixed temperature it depends on the particle size through $D^{-3/2}$, where D is the particle diameter.[15] However, in a dense system the interparticle interactions are expected to modify the magnetic behavior of the assembly. The strength of the dipolar interactions can, in principle, be controlled by varying the particle volumes and their concentration.

In recent experiments an increase of the blocking temperature with particle density has been reported and attributed to dipolar interactions between the particles.[4–10] In contrast to these findings, Mørup and Tronc[11] observed a decrease of the blocking temperature with particle density. Furthermore, the remanence of fine particle assemblies is usually found to decrease due to dipolar interactions,[5–6,10] while increasing values with particle concentration have been reported.[12] Finally, hysteresis measurements showed a decrease of the coercivity with particle density and again this behavior was attributed to dipolar effects.[5,6]

In granular metal solids, the increase of metal volume

fraction leads to the formation of larger particles, which eventually become multidomain. The coercivity as a function of the metal volume fraction in these systems has a peak structure around the percolation threshold.[3] However, as the average interparticle separation decreases, the dipolar interactions play an increasingly important role and the final shape of the H_c versus x_v curve is expected to be modified. Thus, the common attribution of the peak of the $H_c(x_v)$ curve solely to particle-size effects needs reconsideration.

The above-mentioned experimental observations indicate that many open questions remain concerning the way the interparticle dipolar interactions modify the magnetic properties of an assembly of ferromagnetic particles and in particular the remanence, coercivity, and blocking temperature. It is our purpose in this paper to investigate these problems using Monte Carlo simulations. In previous theoretical studies[4,11,16,17] the mean-field approximation was implemented to investigate the role of dipolar interactions in fine particle systems. In particular, Dormann *et al.*[4] predicted an additional energy barrier for the reversal of the particle moment due to the dipolar interactions, while Mørup and Tronc[11] predicted within their model a decrease of the average barrier height. Bertram and Bhatia[16] showed that dipolar effects cause in all cases an increase of the remanent magnetization which can reach the saturation value. Ferré *et al.*[18] studied the hysteresis loop at zero temperature for dilute assemblies of interacting fine particles by a numerical solution of the Landau-Lifshitz-Gilbert equations. Single-particle behavior was obtained when the anisotropy energy was much in excess of the dipolar energy and dipolar interactions alone were shown to induce an anisotropy into the system. In previous Monte Carlo studies, the reduction of remanence due to dipolar interactions was found using a linear chain of Ising spins[19] and the dependence of the coercivity was shown to vary linearly with the metal volume fraction for a weakly dipolar system consisting of a periodic array of dipoles.[20]

Our simulations are more realistic than previous Monte Carlo studies[18,19] in the following aspects: first, three-dimensional classical spins are used, second, the randomness in particle positions is taken into account, and third, the whole range of energy parameters is investigated in order to understand the different behaviors arising from the competition between the anisotropy and dipolar interaction energy. The description of the particle positions as random is a very good approximation in granular solids.[3] In ferrofluids the particles are allowed to move before freezing the system and they tend to form agglomerates with a complicated morphology.[21] The magnetic behavior of the system is sensitive to the microstructure of the agglomerates.[6,21] However, agglomeration can be prevented by coating the particles with a nonmagnetic layer and in this way random structures can be obtained.[10] Therefore, in both kinds of systems the approximation about the random location of particles is justified. It is well known that dipolar forces have directional dependence and consequently their action should be sensitive to the detailed geometrical arrangement of the particles. In particular, spatial randomness is responsible for modifications of the magnetic properties of the system due to ''frozen-in'' local field fluctuations.[22] Another important feature in systems with dipolar interactions is the crucial role played by sample boundaries.[16] We use periodic boundary conditions in order to examine intrinsic properties of the system but also, results for free boundary conditions are presented in order to demonstrate the role of the sample surface. In this work we focus on the study of the remanence and coercivity and their dependence on the growth parameters (particle size and concentration) and the temperature. In a previous work[23] we have studied the coercivity of an assembly with variable concentration of interacting ferromagnetic particles. In this work we extend our previous simulations by studying systems with increasing particle volume. Also the remanence is studied in addition to the coercivity and the role of packing geometry and sample boundaries are investigated.

II. THE MODEL AND THE SIMULATION METHOD

The main information obtained from various preparation methods and magnetic measurements reported in the literature[3–12] can be summarized as follows.

(a) Typical blocking temperatures are well below the Curie temperature and therefore the magnetization density (M_s) of each particle is approximately constant for temperatures up to the blocking temperature.[3] Typical values of magnetization density lie in the range $M_s \sim 500-1500$ emu/cm^3. Thermal fluctuations of the assembly magnetization are well described by a coherent rotation of the magnetic moments of the particles.

(b) Each particle possesses uniaxial anisotropy with an easy axis oriented in a random direction. The anisotropy density (K_1) is an effective value including surface, magnetocrystalline and shape contributions. Typical values of anisotropy constants lie in the range $K_1 \sim 10^5-10^6$ erg/cm^3.

(c) The particles have to a very good approximation a spherical shape. The particle-size distribution can usually be fitted to a logarithmic-normal function with standard deviation $\sigma \sim 0.5-1.5$.[3,5,12] This distribution is very narrow so the system is approximately monodisperse.

(d) The arrangement of particles in space is random.[3,10]

To meet the above experimental requirements we model the particle assembly with a collection of three-dimensional classical spins located at random on the sites of a cubic lattice. Two choices for the lattice geometry (sc and fcc) are used. The magnetostatic interaction between two particles is described via a dipolar field. The total energy for a N-particle system with contributions from uniaxial anisotropy energy, dipolar energy, and external field energy is

$$E=\sum_i \left[g \sum_j \frac{\hat{S}_i \cdot \hat{S}_j - 3(\hat{S}_i \cdot \hat{R}_{ij})(\hat{S}_j \cdot \hat{R}_{ij})}{R_{ij}^3} - k(\hat{S}_i \cdot \hat{e}_i)^2 - h(\hat{S}_i \cdot \hat{H}) \right], \quad (1)$$

where $\hat{S}_i$ is the spin of particle i, $\hat{e}_i$ is the direction of the easy axis of particle i, and R_{ij} is the distance between particles i and j, measured in units of the lattice constant a. Circumflexes indicate unit vectors. The parameters indicating the value of the various energy contributions are $g=(m^2/a^3)$, the dipolar interaction energy, where m is the particle magnetic moment, $k=K_1V$, the anisotropic energy

of a particle with volume V, $h=mH$, the Zeeman energy due to an externally applied field H and $t=k_BT$, the thermal energy. All energy parameters (k,g,h,t) are measured below in arbitrary units. Notice that both g and h depend on the particle volume through the definition of the magnetic moment $m=M_sV$ where M_s is the particle magnetization density.

Experimentally, the composition of a sample containing small magnetic particles in a nonmagnetic binder is described by the metal volume fraction[3,10] defined as the ratio of the volume of the magnetic material to the total volume. Within our nonoverlapping sphere model we define the metal volume fraction as

$$x_v=p\left(\frac{\kappa\pi}{6}\right)\left(\frac{D}{a}\right)^3, \tag{2}$$

where D is the particle diameter, κ is a geometrical factor taking the values $\kappa=1,4$ for the sc and fcc lattice, respectively, and p is the occupation probability of a lattice site by a particle. In a fine-particle system there are two factors determining the importance of dipolar interactions, namely, the average distance between the particles and their size. Our intention here is to study independently these two factors and so we consider two different types of systems.

(a) *Systems with particles of fixed size.* In this model, the number of particles in a certain volume increases without any change in the particle diameter, i.e., x_v increases proportionally to p and D/a is kept fixed, in Eq. (2). The strength of the dipolar interactions changes within this model, solely due to changes in the average interparticle distance. Experimentally, this model corresponds to frozen ferrofluids where the amount of solvent that sustains magnetic particles can be varied.[6,10,11] In granular metal solids, it was shown[3] that the grain size can be varied independently of the metal volume fraction through control of the substrate temperature, but to our knowledge this dependence has not been used so far to produce systems of fixed grain size and variable concentration of particles. Alternatively, application of high pressure on powder samples has been used to vary the average interparticle distance.[5]

(b) *Systems with particles of growing size.* In this model, the particle diameter increases with the metal volume fraction. We assume for simplicity that when we add more magnetic material into a sample of fixed volume, the volume of each particle increases without formation of new particles, i.e., x_v increases proportionally to $(D/a)^3$ and p is kept fixed, in Eq. (2). Within this model, the variation of the dipolar strength is solely due to particle size effects, because the particles are not allowed to move or coalesce during the growth procedure. This approximation is justified only for small values of the metal volume fraction,[3,24] but it preserves the important aspect of the interplay between size effects and dipolar interactions in a granular system.

The equilibrium configuration of the system is obtained from minimization of the total energy of the system using the Monte Carlo technique and the Metropolis algorithm.[25] According to this algorithm a particle is chosen at random, a move of its spin is considered and the change in the energy of the system (ΔE) is calculated. If $\Delta E\leq 0$, the transition to the new state is made and the new configuration is accepted. If $\Delta E>0$, the transition to the new state and the acceptance of the configuration are made with probability equal to $\exp(-\Delta E/k_BT)$. The step of change of the spin direction is adjusted so that approximately 50% of the attempted moves are successful. Finally, thermal averages are obtained from simple arithmetic averages over the accepted configurations.

To obtain the remanence of the assembly we start the simulation with the system initially in the positive saturation state, i.e., all spins along the positive z axis, which is chosen for convenience along one of the cubic axes. The relaxation is performed in zero applied field. The system is assumed to have reached equilibrium after $\sim 10^4$ Monte Carlo steps per spin (MCSS). The average value of the magnetization along the z axis is the required remanence (M_r). To obtain the coercivity the relaxation from the initial positive saturation state along the z axis is performed under an applied field along the negative z axis. The coercivity (H_c) is defined as the applied field at which the magnetization of the sample along the z axis vanishes, within the ''time'' of the simulation, typically $\sim 10^4$ MCSS. Further increase of the number of MCSS up to an order of magnitude ($\sim 10^5$) has not substantially changed our results. This behavior is related to the approximately logarithmic dependence of the magnetization on the observation time that is measured in systems of this type.[26] The determination of the coercive field is achieved by a successive bisection method using the interruption criterion $|M_z|\leq \tau M_s$, with $\tau\sim 0.05$. For a given random sample the values of M_r and H_c are determined and stored. The calculation is repeated keeping all the parameters (system size, occupation probability, particle volume, anisotropy, magnetic moment, and temperature) fixed and changing the configuration of the particles. The final values of the M_r and H_c are obtained from an average over a certain number ($N_c\approx 10-30$) of random configurations.

The system we use for the simulation [Monte Carlo (MC) cell] is a cube of size La ($L=5,6,7$) cut from an infinite sc or a fcc lattice. The particles occupy at random the sites within this cube with probability p. This procedure produces assemblies composed of 30–350 spins, on average. The MC cell is repeated periodically and the Ewald summation technique is implemented to calculate the long range part of the dipolar energy.[27] Satisfactory convergence with the Ewald technique is obtained using $n=2$ repetitions of the central Monte Carlo cell along each of the three Cartesian axes and a Gaussian parameter $\varepsilon=0.3a^{-1}$. As a test of convergence of the Ewald series we calculated the value of the local field at a site of a fully aligned ferromagnetic state of a crystalline ($p=1$) assembly. The theoretical value $H_0=(4\pi/3)M_s$ was reproduced with accuracy 10^{-4}. Considerable computation time is saved if the local fields are stored[28] during the simulation instead of the interaction matrix.[27] However, only relatively small systems (up to $\sim$350 spins) can be studied with reasonable computation effort, because the dipolar interactions have a long range. Typically, for a 7^3 system with $p=0.8$ ($\sim$275 spins) the determination of the average coercive field, within a tolerance of $\tau=0.05$, using 10^4 MCSS and 10 random configurations, required about 3 h CPU time in a DEC Alpha 500.

III. NUMERICAL RESULTS AND DISCUSSION

A. Systems with particles of fixed size

We consider spherical particles of fixed diameter D occupying at random the sites of a simple cubic lattice with lattice

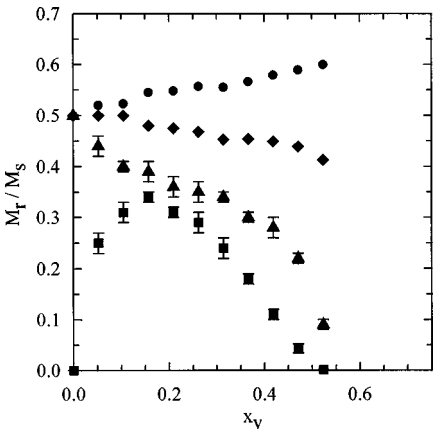

FIG. 1. Remanence as a function of the metal volume fraction for fixed particle size. Random sc packing and periodic boundary conditions. Squares: $k=0$, $g=1.0$, $t=0.001$. Triangles: $k=1.0$, $g=1.0$, $t=0.001$. Circles: $k=4.0$, $g=1.0$, $t=0.001$. Diamonds: $k=4.0$, $g=1.0$, $t=0.001$, and free boundary conditions. Not indicated error bars are of the size of the marks.

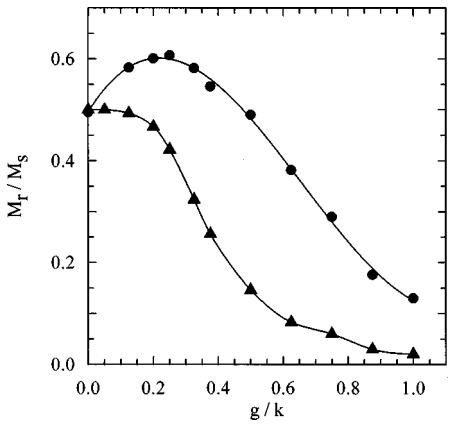

FIG. 2. Remanence as a function of the dipolar interaction strength for an ordered sc array of particles with $k=4.0$, $t=0.001$. Triangles: free boundary conditions. Circles: periodic boundary conditions. Solid lines are guides to the eye. Error bars are of the size of the marks.

constant $a=D$. In Fig. 1 we plot the remanence of the assembly as a function of the metal volume fraction or, equivalently, of the particle density. Three different sets of data are shown that correspond to a weak dipolar system ($g=1.0$, $k=4.0$), a moderate dipolar system ($g=1.0$, $k=1.0$), and a system with dipolar interactions only ($g=1.0$, $k=0$). The data shown in Fig. 1 are results for very low temperatures ($t=10^{-3}$). We notice that the system exhibits very different dependence on the density of particles, depending on the competition between uniaxial anisotropy and dipolar interaction effects. In particular, in a purely dipolar system ($g=1.0$, $k=0$) the remanence shows a maximum for a certain particle density. This behavior can be qualitatively understood as follows: As the concentration of particles increases the system develops an increasing anisotropy that originates from the anisotropic character of the dipolar interactions. This interaction-induced anisotropy is very sensitive to the spatial arrangements of the dipoles and it is maximized around the percolation threshold of the system, which for a sc lattice[29] is $x_c=p_c(\pi/6)\approx 0.157$. This behavior is expected, inasmuch as around the percolation threshold a percolating cluster forms that has a fractal morphology consisting of many chainlike branches. This spatial arrangement of dipoles leads to a nose-to-tail ordering of their magnetic moments[30] and hence to an enhanced magnetization. An analogous enhancement of the dielectric properties close to the percolation threshold has been reported previously[31] for a random assembly of electric dipoles. Increasing the concentration of particles beyond p_c, a three-dimensional system develops that fills up the space and the fractal morphology disappears gradually. In the limit of a fully periodic system, $x_v=(\pi/6)$, the remanence vanishes, in accordance with the theoretical predictions of Luttinger and Tisza,[32] that the ground state of a sc array of dipoles is antiferromagnetic. We examined the equilibrium spin configuration in this limit and we indeed found a columnar antiferromagnetic structure.[27]

Consider next the system with moderate dipolar interactions ($g=1.0$, $k=1.0$) in Fig. 1. For a very dilute system ($x_v\approx 0$) the remanence tends to the theoretical value $M_r/M_s=0.5$ predicted for an assembly of noninteracting ferromagnetic particles with random anisotropy axes.[33] For increasing density of particles, the remanence decreases, indicating that dipolar interactions have on average a demagnetizing effect. Notice that this decrease is highly nonlinear and is more abrupt close to the limit of an ordered array of spheres.

Finally, for a weakly interacting system ($g=1.0$, $k=4.0$) a qualitatively different behavior is seen. In particular, the remanence increases with particle concentration. This behavior is not observed if free boundary conditions are used instead of periodic ones. In a sample with free boundaries a continuous reduction of the remanence occurs, as shown also in Fig. 1. This reduction of M_r is attributed[27] to the demagnetizing field arising from the free magnetic poles forming at the surface of the sample. However, the absence of a demagnetizing field, as for example in a periodically repeated system, does not necessarily imply that the dipolar interactions cause an increase of the magnetization. It is only within a certain range of the interaction strength that an increase is obtained, as Fig. 1 indicates. To estimate this range, we show in Fig. 2 results for the low-temperature ($t=10^{-3}$) magnetization of a periodic array of dipoles with and without free surfaces. We can be deduce from Fig. 2 that the interactions cause a magnetization enhancement in the range up to $g/k\sim 0.5$, while stronger interactions lead to a serious reduction of the magnetization. A similar effect of the sample boundaries on the remanence is also expected if the dipole positions are random instead of periodic, but in this case the effect will be weaker because the average interparticle distance is bigger in the randomly diluted system. This behavior is indeed observed for the weakly dipolar system in Fig. 1.

Bertram and Bhatia[16] predicted within a mean field calculation for an infinite random system, that increasing dipolar interactions result in a continuous increase of the remanence up to the saturation value. Our simulations indicate that the saturation value cannot be reached for an infinite sample, but instead a maximum remanence of about $0.6M_s$ occurs for weak dipolar strength, followed by a drop of the values. This qualitative difference occurs because in the mean field approximation the near field of each dipole is not considered. The latter is responsible for the drop of the magnetization for strong couplings.

Luo *et al.*[10] performed magnetization measurements on frozen ferrofluids containing Fe_3O_4 particles. The authors estimated that in their samples the dipolar strength (m^2/D^3) was slightly larger than the anisotropy energy (K_1V) and they found a remanence $M_r/M_s \sim 0.2$ at very low temperatures. To compare with these experiments, we define within our model $a=D$ and choose $g/k \sim 1.0$. For this energy ratio ($g/k \sim 1$) our simulations produce a similar reduction of the remanence at low temperatures (Fig. 1) in agreement with these measurements. Mørup *et al.*[12] reported an increase of the remanence with increasing particle interactions for a frozen ferrofluid containing Fe_2O_3 particles. The parameters reported for these particles correspond to a ratio $g/k \sim 0.34$. The authors reported an increase of the remanence under the application of external pressure to the sample. Since application of pressure is equivalent to an increase of the particle density we find that for this value of g/k the observed increase of the remanence is predicted within our simulations (Figs. 1 and 2).

To gain a better physical insight into the way the dipolar interactions affect the magnetization, we consider a dipole-pair model. Let the spins be located on the x axis and assume single-particle uniaxial anisotropy along the random axes $\hat{e}_1$ and $\hat{e}_2$. The energy of the pair is

$$E = g[\hat{S}_1 \cdot \hat{S}_2 - 3(\hat{S}_1 \cdot \hat{R})(\hat{S}_2 \cdot \hat{R})] - k[(\hat{S}_1 \cdot \hat{e}_1)^2 + (\hat{S}_2 \cdot \hat{e}_2)^2], \quad (3)$$

where $\hat{R} = \hat{x}$ is the bond direction. Let the pair be initially saturated in the positive z direction and the applied field be gradually switched off. If the spins are not coupled ($g=0$), the system is known to have a remanence $M_r/Ms = 0.5$.[33] If, now, the spins are coupled, the first term in Eq. (3), namely, $g\hat{S}_1 \cdot \hat{S}_2$, has an isotropic antiferromagnetic character, while the second one, $-3g(\hat{S}_1 \cdot \hat{R})(\hat{S}_2 \cdot \hat{R})$, an anisotropic character favoring ferromagnetic alignment along the bond axis. Therefore, a weak finite coupling ($g>0$) causes a decrease of the remanence, because both dipolar terms in Eq. (3) act against the ferromagnetic order along the z axis. For an assembly of N dipoles this argument can be used to explain the continuous decrease of magnetization with dipolar strength. Alternatively, the same behavior is explained on macroscopic grounds, using the concept of the demagnetizing field. To understand the observed increase of magnetization for an infinite system, we consider a dipole pair with periodic boundary conditions. The magnetization of each pair is $\mathbf{M} = (m/2V_t)(\hat{S}_1 + \hat{S}_2)$, where V_t is the total volume per particle. Due to the periodic conditions, $\mathbf{M}$ is also the magnetization of the medium surrounding the central pair. The energy of the central dipole-pair has an extra energy contribution due to the Lorentz field $E_L = -N_d m(\hat{S}_1 + \hat{S}_2) \cdot \mathbf{M}$, where N_d is an appropriate demagnetizing factor depending on the assumed shape of the central dipole. If we exclude self-interaction terms, the dipolar energy of the central pair can be written as

$$E_{\mathrm{dip}} = (g-d)(\hat{S}_1 \cdot \hat{S}_2) - 3g(\hat{S}_1 \cdot \hat{R})(\hat{S}_2 \cdot \hat{R}), \quad (4)$$

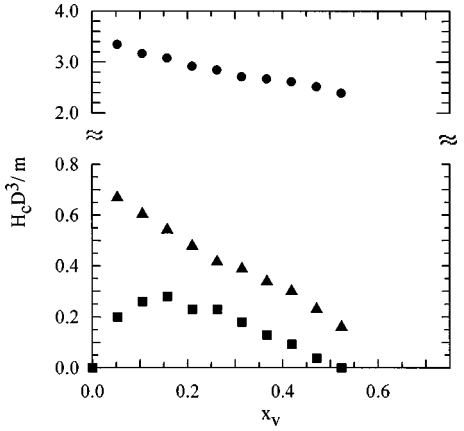

FIG. 3. Coercivity as a function of the metal volume fraction for fixed particle size. Random sc packing and periodic boundary conditions. Squares: $k=0$, $g=1.0$, $t=0.001$. Triangles: $k=1.0$, $g=1.0$, $t=0.001$. Circles: $k=4.0$, $g=1.0$, $t=0.001$. Error bars are of the size of the marks.

with $d = N_d m^2/V_t$. Equation (4) implies that the surrounding medium reduces the strength of the first term in Eq. (3) that favors antiferromagnetic ordering of the spins, or equivalently, the ferromagnetic character of the coupling is enhanced. Consequently, an increase of the magnetization above the noninteracting value is achieved. When the dipolar strength g is large, the antiferromagnetic character of the first term in Eq. (4) is restored ($g-d>0$) and a decrease of the magnetization occurs.

Next we consider the coercivity of the assembly. In Fig. 3 we plot the coercivity for the same parameters as in Fig. 1. For a system composed of isotropic dipoles ($g=1.0$, $k=0$), the coercivity shows the characteristic peak around the percolation threshold. The system, in this region is strongly anisotropic due to the chainlike structure of the backbone of particles. For a weakly dipolar system ($g=1.0$, $k=4.0$) the coercivity decreases following Néel's prediction, namely, a linear decrease of the coercivity with the particle concentration $H_c(p) = H_c(0)(1-p)$.[33] However, the coercivity of the fully ordered sample is not zero, as this formula suggests, but has a finite value. In other words the interactions do not completely cancel the blocking effects due to the uniaxial anisotropy. In the intermediate case, moderate dipolar interactions ($g=1.0$, $k=1.0$) cause a substantial decrease of the coercivity, but deviations from Néel's linear law start to develop. We also found that the decrease of coercivity with the strength of interactions is a common feature of both infinite and finite samples (data for the latter case are not shown here) and that finite samples exhibit always slightly smaller ($\sim$10% for $g/k \sim 1$) values of H_c, than the corresponding infinite ones.

If we compare the behavior of the coercivity with this of the remanence for various particle densities, it is interesting to notice that for strong ($g/k \gg 1$) and moderate ($g/k \sim 1.0$) dipolar strengths these magnetic properties show a similar dependence on the particle density. Only in infinite systems with weak dipolar interactions ($g=1.0$, $k=4.0$) is a decrease of the coercivity accompanied by an increase of the remanence. Referring back to Eq. (4), we believe that this behavior stems from the fact that the presence of an infinite surrounding medium does not directly affect the anisotropic part

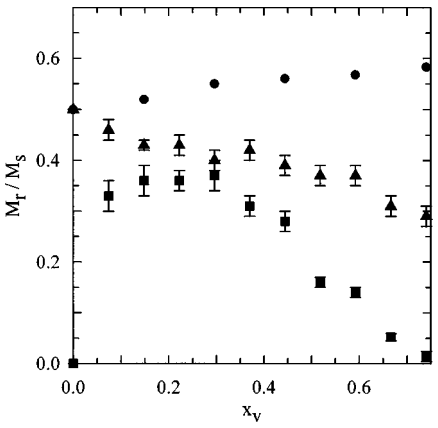

FIG. 4. Remanence as a function of the metal volume fraction for fixed particle size. Random fcc packing and periodic boundary conditions. Squares: $k=0$, $g=1.0$, $t=0.001$. Triangles: $k=1.0$, $g=1.0$, $t=0.001$. Circles: $k=4.0$, $g=1.0$, $t=0.001$. Not indicated error bars are of the size of the marks.

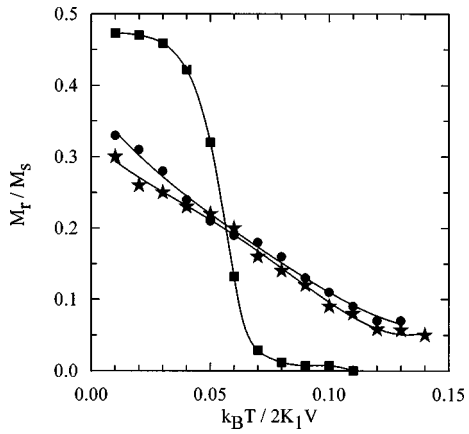

FIG. 6. Temperature dependence of remanence. Random sc packing and periodic boundary conditions. Squares: $k=1.0$, $g=0$. Circles: $k=1.0$, $g=1.0$, and $x_v=0.157$ ($p=0.3$). Stars: $k=1.0$, $g=1.0$ and $x_v=0.314$ ($p=0.6$). Solid lines are guides to the eye. Error bars are of the size of the marks.

of the dipolar energy, which contributes to the hysteresis behavior of the system. Therefore, the boundary conditions, or in other words the macroscopic demagnetizing field, have a stronger effect on the magnetization of the assembly than on the coercivity.

In order to investigate the role of the packing geometry of the particle assembly we show in Figs. 4 and 5 the remanence and coercivity, respectively, for particles occupying at random sites of an fcc lattice. The values of parameters characterizing the particles (M_s, K_1, V) and the temperature are the same with the corresponding cases in Figs. 1 and 3. There is an overall similarity between the results for an fcc and sc lattice. There are two points to mention, though. First, notice that a periodic system ($p=1$) composed of isotropic dipoles ($g=1.0$, $k=0$) has zero remanence and coercivity, while it is known that the ground state of an fcc array of dipoles is ferromagnetic.[32] This situation occurs because of domain formation in the Monte Carlo cell which is finite. An examination of the equilibrium spin configuration for the ordered sample showed a formation of closure domains parallel to the faces of the cubic cell. The second point to mention is that the fcc packing leads to slightly higher magnetization and coercivity than the sc. This effect is more pronounced in the dense limit ($x_v > 0.3$) and in systems with moderate and strong ($g \geq k$) dipolar interactions. We attribute this behavior to the increasingly important role of the dipolar interactions that favor a ferromagnetic alignment for dipoles on an fcc lattice.

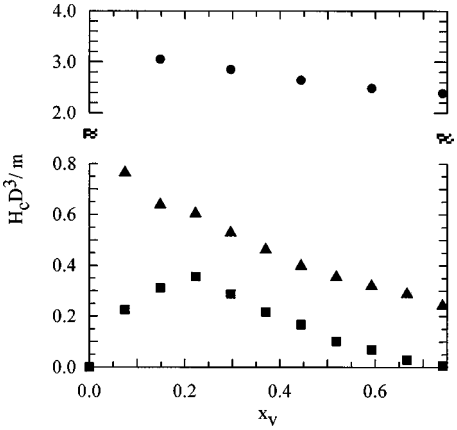

FIG. 5. Coercivity as a function of the metal volume fraction for fixed particle size. Random fcc packing and periodic boundary conditions. Squares: $k=0$, $g=1.0$, $t=0.001$. Triangles: $k=1.0$, $g=1.0$, $t=0.001$. Circles: $k=4.0$, $g=1.0$, $t=0.001$. Error bars are of the size of the marks.

The superparamagnetic relaxation time for an assembly of noninteracting particles follows the predictions of the Néel-Brown theory,[32] namely, $\tau=\tau_0 \exp(K_1 V/kT)$, where τ_0 is a characteristic time of the system. As the temperature raises the relaxation over the anisotropy barrier ($K_1 V$) becomes faster. The blocking temperature ($T_B^{(0)}$) is defined as the temperature above which the particle has enough time, within the observation time, to reverse its magnetization. Clearly, $T_B^{(0)}$ is dependent on the method used to observe the relaxation and is given by[15] $kT_B^{(0)}=K_1 V/\lambda$, where $\lambda=\ln(\tau_{\rm obs}/\tau_0)$ and $\tau_{\rm obs}$ is the observation time. For noninteracting particles the dependence of remanence on the temperature is shown in Fig. 6. Also, the coercivity for a noninteracting assembly with random anisotropy follows the well-known relation[15]

$$H_c(T)=0.48H_K[1-(T/T_B^0)^{1/2}], \tag{5}$$

where $H_K=2K_1/M_s$. This temperature dependence of the coercivity for a noninteracting assembly is reproduced with the Monte Carlo simulation in Fig. 7. When the dipolar interactions ($g/k=1$) are switched on an interesting behavior is seen. At temperatures much lower than the blocking temperature $T_B^{(0)}$, both the magnetization and the coercivity are substantially reduced relative to the noninteracting case. As the temperature rises, a much slower decay of both the remanence and the coercivity is seen, relative to the noninteracting system. Most importantly, the dipolar assembly retains the ferromagnetic character at temperatures much higher than $T_B^{(0)}$. From the data shown in Figs. 7 and 8 an approximate increase of $T_B \sim 2T_B^{(0)}$ is estimated for a system with moderate interactions ($g/k \sim 1$). Luo *et al.*,[10] who per-

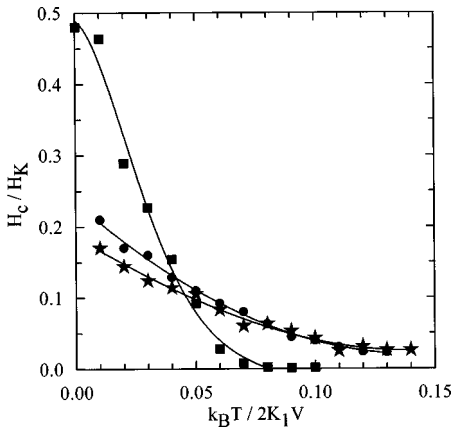

FIG. 7. Temperature dependence of coercivity. Random sc packing and periodic boundary conditions. Squares: $k=1.0$, $g=0$. Circles: $k=1.0$, $g=1.0$, and $x_v=0.157$ ($p=0.3$). Stars: $k=1.0$, $g=1.0$, and $x_v=0.314$ ($p=0.6$). Solid lines are guides to the eye. Error bars are of the size of the marks.

formed experiments on frozen ferrofluids and Dormann *et al.*,[4] who used a granular system Fe/Al_2O_3, reached similar conclusions about the increase of the blocking temperature due to dipolar interactions. Our results shown in Figs. 7 and 8, for $T>T_B^{(0)}$ support the mean field model presented by these authors,[4] in order to explain the high-temperature (superparamagnetic) behavior of the granular system. In the high-temperature regime the dipolar interactions introduce an additional energy barrier for the reversal of the particle moments, as the authors of Ref. 4 assumed, that gives rise to nonzero values of the coercivity. However, for $T<T_B^{(0)}$ this model cannot explain the demagnetizing role played by the dipolar interactions, which is manifested by the drop of the M_r and H_c values below the noninteracting case. In contrast to the above measurements, Mørup *et al.*[11] observed a decrease of the blocking temperature in dense samples. Our simulations indicate that dipolar interactions among single-domain ferromagnetic particles cannot account for such a decrease. As far as the random field model implemented by the same authors[11] to support their experimental findings is concerned, we believe that it misses the important aspect of the temporal fluctuations of the local field. We have tested this idea by using a static random local field in our simulations instead of the true dipolar field and the outcome was indeed a decrease of the blocking temperature with the strength of the interactions.

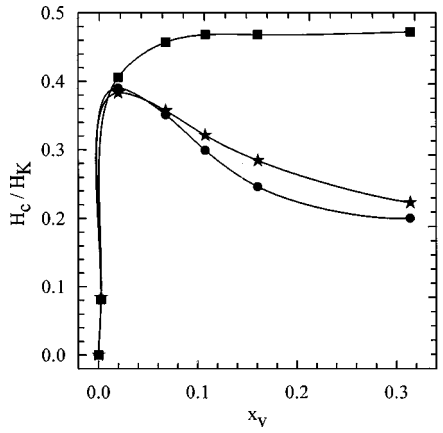

FIG. 8. Coercivity as a function of the metal volume fraction for a system with growing particle volume at very low temperature $t=0.001$. Squares: sc packing, $k=(D/a)^3$, $g=0$. Circles: sc with periodic boundary conditions (PBC's), $k=(D/a_1)^3$, $g=(D/a_1)^6$. Stars: fcc with PBC's, $k=(\sqrt{2}D/a_2)^3$, $g=(\sqrt{2})^3(D/a_2)^6$. Solid lines are guides to the eye. Error bars are of the size of the marks.

B. Systems with particles of growing size

We consider next systems where the particle volume increases linearly with the metal volume fraction. For an assembly of identical noninteracting ferromagnetic particles Eq. (5) also gives the dependence of the coercivity on the particle volume for a fixed temperature

$$H_c(x_v)=0.48H_K[1-b(T)x_v^{-1/2}], \tag{6}$$

with $b(T)=(\lambda k_B T p\kappa/K_1 a^3)^{1/2}$. Thus, at a finite temperature, there is a minimum value of the metal volume fraction below which the coercivity of the assembly vanishes and the system becomes superparamagnetic. Above this threshold the coercivity of the sample increases and makes a plateau approaching the value $0.48H_K$. In order to allow for the particle volume to increase without violating the condition for nonoverlapping spheres that our geometrical model assumes, the energy parameters are written as $g=g_0(D/a)^6$, where $g_0=M_s^2\pi^2a^3/36$ and $k=k_0(D/a)^3$, where $k_0=K_1\pi a^3/6$. The ratio D/a varies in the range (0,1) for the sc packing and (0, $1/\sqrt{2}$) for the fcc packing. It is therefore clear that as the particle diameter grows, both parameters g, k increase, but the dipolar energy grows faster than the anisotropy energy. We study a system with moderate dipolar strength, so we choose $g_0=k_0=1.0$.

In Fig. 8 we show the dependence of the coercivity on the metal volume fraction at a very low temperature ($t=10^{-3}$). For noninteracting particles Eq. (6) is reproduced with the characteristic plateau. When interparticle interactions are introduced, a competition between size effects that produce an increase of the coercivity and the dipolar interactions that act in the opposite way, leads to a peaked structure for the $H_c(x_v)$ curve and a serious reduction of the plateau value. The drop in the plateau value is larger in more dense systems. For example, for $x_v=0.16$ ($p=0.3$ and $D=a$) a 40% reduction is found (not shown here), while a reduction of 60% is seen in Fig. 8 for $x_v=0.32$ ($p=0.6$ and $D=a$). We also compare in Fig. 8 the coercivities of two cubic samples of the same size ($L_1a_1=L_2a_2$) containing an equal number of particles characterized by the same parameters (M_s,K_1,D), but having different packing geometries. The packing geometry seems to modify the result in a minor way (~10%) and once again fcc packing leads to an enhanced coercivity relative to sc.

At higher temperatures ($t=0.04$), the $H_c(x_v)$ curves (Fig. 9) lie below the corresponding ones for low temperature (Fig. 8) and the interactions cause a smaller (~50%) reduction of the maximum coercivity. Also, the peak in the coercivity of the interacting assembly observed at very low temperature (Fig. 8) is absent now, because thermal fluctuations act against the delicate competition between anisotropy and dipolar interactions which produced that peak. Notice

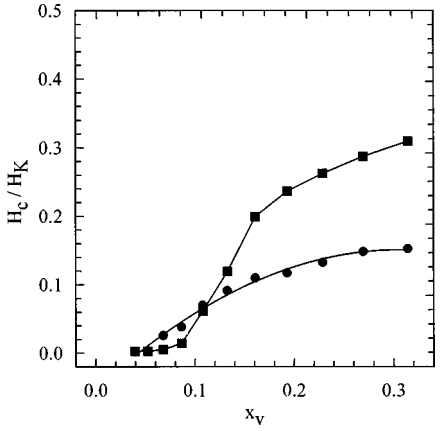

FIG. 9. Coercivity as a function of the metal volume fraction for a system with growing particle volume at higher temperature $t=0.04$. Squares: sc packing, $k=(D/a)^3$, $g=0$. Circles: sc with PBC's, $k=(D/a)^3$, $g=(D/a)^6$. Solid lines are guides to the eye. Error bars are of the size of the marks.

also that the interactions shift the critical volume downwards, below which superparamagnetism is observed. This is indicated by the crossing of the two curves in Fig. 9. In other words, particles with small volumes ($x_v<0.1$) are superparamagnetic ($H_c\approx 0$) if they are noninteracting while they have a nonzero coercivity if they interact via dipolar forces. A similar conclusion was drawn by an examination of the temperature dependence of the coercivity in Fig. 7. Experimentally, larger coercivities are obtained in granular solids by increasing the metal volume fraction[3] that leads to formation of larger particles. The maximum H_c value is obtained before multidomain formation starts within each particle. The conclusion drawn from Figs. 8 and 9 is that the maximum coercivity measured experimentally is substantially reduced (30–60 %) relative to the predictions of the single particle theory due to dipolar interactions among the grains. This result raises a flag of caution about the interpretation of the experimental findings by means of the theory for noninteracting particles.

IV. CONCLUSIONS

We have studied the remanence (M_r/M_s) and the coercivity (H_c) of a monodisperse assembly of randomly located uniaxial ferromagnetic particles interacting with dipolar forces. The magnetic properties of the system are determined by the interplay of the single-particle anisotropy energy (k) and the dipolar interaction energy. The latter is a function of the particle density or metal volume fraction (x_v) and the dipolar energy strength (g). The main features of the magnetic properties are summarized below.

(a) In purely dipolar systems ($g\neq 0$, $k=0$) at low temperatures, both the remanence and coercivity approach zero in the limit of extreme dilution and in the limit of a fully periodic array of (nonoverlapping) spherical particles. Both magnetic properties are maximized close to the percolation threshold, due to the fractal morphology of the assembly structure. Similar behavior is expected for strongly dipolar systems ($g/k\gg 1$).

(b) In systems with moderate dipolar couplings ($g/k\sim 1$) at low temperatures, both the remanence and magnetization decrease with particle density.

(c) In weakly dipolar systems ($g/k<1$) at low temperatures, an increase of the remanence is accompanied by a drop of the coercivity with particle density. The increase of the magnetization is a mean-field effect of the dipolar interactions caused by the macroscopic Lorentz field. This field has only a minor effect on the coercivity of the system, because it modifies only the isotropic part of the dipolar near field.

(d) Dipolar interactions ($g/k\sim 1$) cause a slower decay of the remanence and coercivity with temperature.

(e) At high temperatures, $T>T_B^{(0)}$, dipolar interactions preserve the magnetic character of the assembly and lead to an increase of the blocking temperature of the system.

(f) Within the assumption of linear growth (i.e., the particle volume increases proportionally to the metal volume fraction) the maximum value of the coercivity appears substantially reduced ($\sim$50–60 % for $g/k\sim 1$) relative to the predictions for noninteracting particles.

(g) The packing geometry of the particles has a small effect on the magnetization and coercivity at very low temperatures. fcc packing produces up to 10% higher values than the sc packing for systems with moderate interactions ($g/k\sim 1$).

(h) The presence of sample free boundaries reduces the coercivity and the magnetization of the interacting assembly relative to the corresponding values for the infinite sample. This effect is much more pronounced in the magnetization than in the coercivity.

The work in this paper has focused on monodisperse systems. This is a reasonable approximation for a number of experimental studies.[34] With a broader size distribution the behavior in the case of noninteracting particles can be obtained by a convolution with the size distribution function. If interactions are present it is necessary to introduce the size distribution in the simulation cell. It is likely that a simple convolutions would overestimate the broadening effects.

In order to discuss experimental findings, the state of nanosized magnetic particles is often described, at low temperatures, as blocked or collective and, at high temperatures, as superparamagnetic. Within our approach, there is no necessity for making *a priori* assumptions about the particles state. However, it is likely that the low concentration and strong anisotropy regime relates to the blocked state and the high concentration and weak anisotropy regime relates to the collective state.[35] A manifestation of the low-temperature collective behavior is the peak in the concentration dependence of the remanence and coercivity around the percolation threshold (e.g., Fig. 1). Although this behavior is maximized for magnetically isotropic particles, a reminiscent of it was shown to occur up to anisotropy energies comparable to the dipolar strength.

ACKNOWLEDGMENTS

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