Magnetic properties of a frozen ferrofluid: Local-mean-field theory

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(Received 17 January 1994)

Recent experiments on the magnetic properties of frozen ferrofluids indicate clear deviations from canonical spin glass behavior. To elucidate these differences we present simulations based on a local-mean-field theory approach. This theoretical scheme was previously found to be quite successful for traditional spin glass and random field systems. In a parallel fashion we study frustration effects associated with a magnetic dipole-dipole interaction for a random spatial arrangement of Heisenberg spins in a quenched ferrofluid. Some of the experimental features can be reproduced if the spins are assumed to be inhomogeneously distributed in space.

Glassy behavior in magnetic systems has received considerable attention over the past two decades. Frustration associated with Ruderman-Kittel-Kasuya-Yosida interactions among impurity spins in nonmagnetic hosts leads to metallic spin-glass behavior, in which the magnetization at a given temperature T and field H depends on the order in which T and H are cycled. Diluted antiferromagnets display a similar degree of history sensitivity with the new possibility of history-dependent long-range order. Recent studies[1] of frozen ferrofluids have added another member to the class of frustrated systems. Here the frustration arises from dipole-dipole interactions between ferromagnetic microcrystals which are randomly situated in space. In this paper we study this quenched ferrofluid using a mean-field simulation technique which has been widely applied to other glassy systems. Of particular interest is the behavior of the field-cooled (FC) and zero-field-cooled (ZFC) magnetizations, which are found experimentally to be different from their spin-glass analogs.

Our physical picture of irreversibility derives from the evolution with H and T of metastable states on the free-energy surface.[2,3] Here the free energy F is assumed to be a function of N variables associated with the average magnetization m_i of N spins in the system. The self-consistent equations for the N-dimensional minima are derived from the simplest (local) mean-field theory, although more sophisticated functionals have been tried with less success. The system is prepared in a given state, say at high temperatures and the temperature is then lowered in the presence (FC) or absence (ZFC) of a field. Upon warming or changing H a given minimum may disappear and the system will then fall irreversibily into a nearby state. An iterative solution of the mean-field equation $\partial F/\partial m_i = 0$, captures the physics of this irreversible behavior. For the spin-glass and random-field (or diluted antiferromagnet) systems this procedure has been found to yield results for the various history-dependent magnetizations which are remarkably similar to those measured experimentally.

Recent attention has focused on the quenched ferrofluid because (a) it provides an opportunity for studying frustration associated with dipole-dipole interactions at experimentally accessible temperatures and (b) provides a system in which there is random anisotropy along with these competing (dipolar) exchange interactions. In these studies[1] Fe_3O_4 magnetite particles of size 50 ± 16 Å, are suspended in nonmagnetic hydrocarbon oil. To avoid clustering each particle is coated with a ~20-Å layer of nonmagnetic surfactant. Becuase of the large size of the ferrimagnetic microcrystal the average magnetic moment of each particle is $\sim 3000 \mu_B$. In this way the characteristic dipole interactions $J_{ij} = \mu_i \mu_j (1 - 3\cos^2\theta_{ij})/r_{ij}^3$ are moved from the mK to the K temperature range. For temperatures below 100 K the system develops a uniaxial easy axis, which upon freezing will be fixed in a random orientation.

While this work was in progress, we learned of a related attempt to address the ferrofluid experiments within the same local-mean-field method. Załuska-Kotur and Cieplak[4] modeled the ferrofluid as an Ising system on a lattice, with only nearest-neighbor interactions having couplings distributed according to a Gaussian curve. The random axes were assumed to be uniformly distributed. Not surprisingly, they found behavior which was essentially indistinguishable from a canonical spin glass. By contrast, there are two features of the experiments which we chose to focus on, both of which deviate from their counterparts in spin glasses:

(i) Field-cooled and zero-field-cooled magnetizations depart from each other at a temperature $T_d \gg T_{\max}$, where $T_{\max}$ is the temperature at which the ZFC magnetization has a maximum.

(ii) The FC magnetization shows no saturation upon freezing. This is very different from the behavior in spin glasses, where the FC magnetization saturates below the freezing temperature.

Here in contrast to the Ising model on a lattice used in Ref. 4, we investigate the more physically appropriate case of Heisenberg spins distributed randomly in space.

The Hamiltonian is given by

$$\mathcal{H}=J\sum_{i,j}J_{ij}\mathbf{S}_i\cdot\mathbf{S}_j-\sum_i\mathbf{S}_i\cdot(\mathbf{H}+\mathbf{B}_i)\ . \tag{1}$$

The coupling J_{ij} is the dipole-dipole interaction, given by $J_{ij}=\mu_i\mu_j(1-3\cos^2\theta_{ij})/r^3$. All distances are rescaled by the particle diameter, which determines the value for the exchange interaction $J\approx 32.5$ K. To reduce computer time, only those dipole-dipole interactions were included if the pairs were within four average nearest-neighbor distances. If the distance exceeded this cutoff, the interactions were taken to be zero. However, with the periodic boundary conditions this included the majority of the particles. In Eq. (1), $\mathbf{H}$ is the external magnetic field, and the effect of the frozen-in easy axis is simulated by a local magnetic field $\mathbf{B}_i$, where the direction of this local magnetic field is randomly chosen for each particle. The length and direction of the thermally averaged local magnetic moment $\mathbf{m}_i$ is determined self-consistently from the equation

$$\mathbf{m}_i=\mathbf{H}_i\frac{SB_s(|\mathbf{H}_i|)}{|\mathbf{H}_i|}\ , \tag{2}$$

where the total molecular field (without rescaling) is given by

$$H_i^\mu\equiv\beta\sum_{j,\nu}J_{ij}^{\mu\nu}m_j^\nu+\beta(H\delta_{\mu z}+B_i^\nu) \tag{3}$$

with $\beta^{-1}=k_BT$, and the external magnetic field applied in the $\hat{z}$ direction. Here B_s is the Brillouin function for spin S.

To probe the effects of dilution we positioned the particles using a molecular-dynamical routine. Because the particles have a finite volume, and therefore a minimum separation, it is inappropriate to place the particles randomly in space. This would give rise to unphysical interactions from pairs of particles which were too close. One simple way to overcome this problem is to place the particles randomly in space with a constraint that no two particles are closer than some preset distance. An alternative method is to placed the particles in a simulation cell of length L and allow them diffuse subject to a specified interaction potential. For the volume fractions of interest for the present study (less than 10%) the main effect of these interactions is to avoid overlap. Therefore one can use a purely repulsive interaction with a hard core with either a Monte Carlo method or molecular dynamics. We adopted the latter along with a Lennard-Jones interaction truncated at $r_c=2^{1/6}\sigma$, where σ is the usual distance scale for Lennard-Jones particles. Since the volume fraction $\phi=\frac{4}{3}\pi\sigma^3/L^3$ was less than 0.10, the particles were initially placed on a simple cubic lattice to avoid overlap and the simulation was run until the particles had diffused over a distance many times their own radius. These simulations were run at a temperature $T=\epsilon$, where ϵ is the strength of the Lennard-Jones interaction. Because the particles were dilute, they were coupled weakly to a heat bath. This achieved rapid equilibration.[5] After equilibration, configurations of the particles were saved and the positions of the particles frozen and used in the ZFC and FC studies. Additional configurations for the particles were obtained simply by running the simulation longer. Once a configuration of the spins is determined, the mean-field equations are iterated until convergence (to an accuracy of 10^{-6}) is achieved. Generally this required 100 iterations for a system with $N=800$. Because of the limitations of computer memory we did not study larger systems, although a few runs with 1500 particles were considered, which led to similar results. We used temperature steps $\Delta T=10$ K for cooling and $\Delta T=2.5$ K for heating. Even with systems of this moderately large size, we had difficulty treating low external magnetic fields. Finite-size effects were most apparent upon cooling in zero field, and subsequent application to a lower field. Here, if this ZFC state is generated with temperature steps that are too large, the resulting magnetizations before and after field application may be comparable. To avoid these sources of error we decreased the temperature steps for cooling to $\Delta T=2$ K when $T<100$ K for external magnetic fields $H<50$ G. Even then the ZFC magnetization after cooling could be as large as 10% of the ZFC magnetization with the external magnetic field turned on. Whenever this was the case we chose to disregard the simulation. Because of these finite-size effects, for the most part we limited our consideration to fields $H\approx 25$ G.[6] In contrast to the external field the local magnetic field $\mathbf{B}_i$ was usually taken to be ≈ 10 G.[7] A typical result of our simulations is shown in Fig. 1 (all figures are obtained by averaging over two

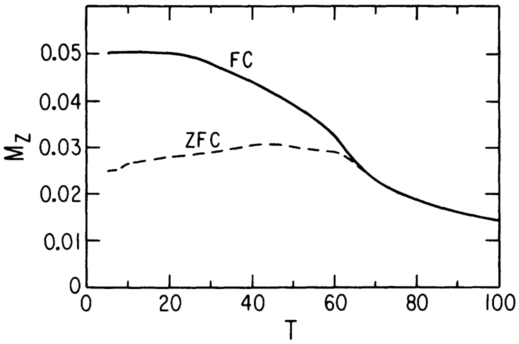

FIG. 1. The FC (solid curve) and ZFC magnetization (dashed) for an ensemble of 800 particles, with an external magnetic field of 25 G, a random local magnetic field of 10.0 G. The particle volume fraction $\phi=0.10$.

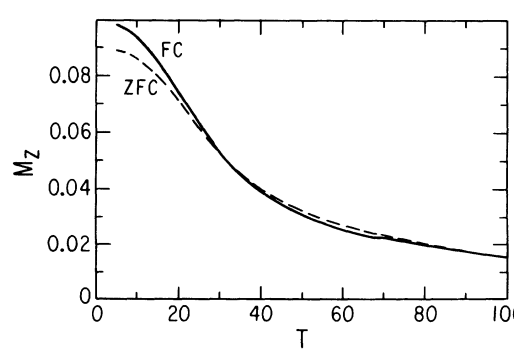

FIG. 2. The FC (solid curve) and ZFC magnetization (dashed) for a more diluted system with volume fraction $\phi=0.01$. The number of particles is 800, $H=25$ G, $H_i=10$ G.

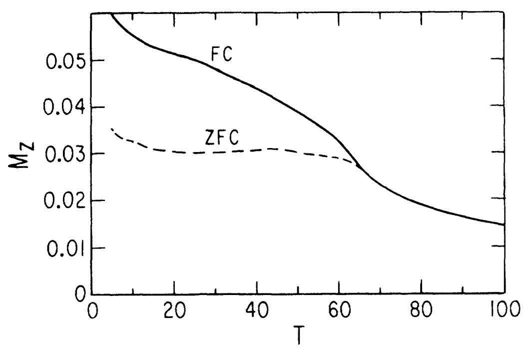

FIG. 3. The FC (solid curve) and ZFC magnetization (dashed) for a 95–5 % mixture of volume fractions $\phi=0.10$ and $\phi=0.01$. The number of particles is 800, $H=25$ G, $H_i=10$ G.

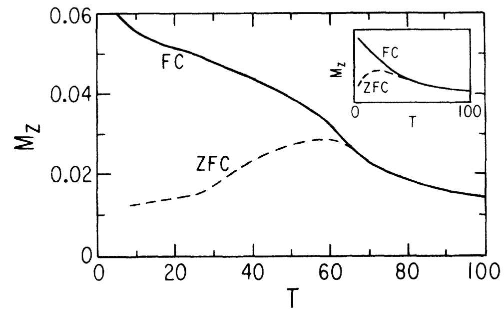

FIG. 4. The FC (solid curve) and an estimate of the ZFC magnetization (dashed) when an additional Dzyaloshinsky-Moriya anisotropy is added to the model for a 95–5 % mixture of volume fractions of 10 and 1 %. The number of particles is 800, $H=25$ G, $H_i=10$ G.

runs).

Here the FC (solid) and ZFC (dashed) magnetizations are plotted as a function of temperature for 800 spins in an external magnetic field of 25 G, and the volume fraction $\phi=0.10$. These results are essentially identical to those obtained for random short-range interactions in nearest-neighbor Heisenberg spin glasses with uniaxial anisotropy. For spin glasses, in the Ising limit, or when an anisotropy of the Dzyaloshinsky-Moriya form is used, the ZFC magnetization tends to be affected more by the frustration so that it decreases with decreasing temperature. By contrast in the isotropic Heisenberg case, the FC and ZFC magnetizations are essentially identical. Similar results are expected for the frozen ferrofluid. Thus the absence of a downturn in the ZFC magnetization is presumably a consequence of the Heisenberg model. This difference can be seen by comparing with the Ising calculations of Ref. 4. To probe the effects of dilution we studied the same simulation for a volume fraction $\phi=0.01$ as shown in Fig. 2.

In order to obtain a nonzero splitting between the ZFC and FC curve, we increased the coupling J from 32.5 to 100 K. As expected in the dilute limit, interaction (as well as frustration) effects are weak. As a consequence the FC curve continues to rise with decreasing temperature, as for almost free spins.

Comparing both figures with experiment, it seems evident that the observed behavior represents a mixture of the effects obtained with the two concentrations simultaneously. The absence of saturation in the FC magnetization suggests that there is a fraction of nearly free spins in the sample which are not subjected to frustration effects. At the same time there is significant splitting between the FC and ZFC results so that some degree of frustration is present, at least among a significant fraction of the spins. It may be conjectured, then, that the most reliable simulation of the ferrofluid should be based on an inhomogeneous picture in which there is a mixture of dilute and moderate concentrations.

To simulate a ferrofluid with this extrinsic inhomogeneity, we compute a weighted average of results obtained for volume fractions $\phi=0.10$ and $\phi=0.01$.[8] For definiteness we show in Fig. 3 an example in which the two concentrations are distributed in a 95–5 % mixture.

While this figure captures some features of the experimental data, better consistency is obtained when additional anisotropy is included. In Fig. 4 we show an estimate which includes the effect of Dzyaloshinsky-Moriya anisotropy. This figure was obtained from earlier work on short-range Heisenberg spin glasses[3] and provides an estimate of the splitting of the two magnetizations as a function of temperature. This splitting was superimposed on the ferrofluid results. As a check on this procedure, we demonstrated that it qualitatively reproduces the standard Ising results.

For comparison we plot the experimental results of Ref. 1 in the inset. It appears that agreement is reasonable in most features. Nevertheless the splitting of the maximum in the ZFC magnetization and the irreversibility temperature are not as evident in the simulations as they are in the data.

In conclusion, we have performed mean-field simulations of a quenched ferrofluid of Heisenberg spins. The behavior of the irreversible magnetizations measured experimentally can be accounted for provided there is both inhomogeneity in the system as well as some anisotropy which can be taken, for example, to be of the Dzyaloshinsky-Moriya type. Only in this way, can one understand behavior which is different from that observed in canonical spin glasses.

This work was supported under Grant No. NSF-DMR-88-19860. We acknowledge useful conversations and assistance from A. Baljon and T. F. Rosenbaum.

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[6] This is somewhat larger than those considered experimentally. The only effect is that T_{max} will be a little larger.
[7] There is hardly a noticeable effect when the magnitude of this field is lowered to, e.g., 1 G. Serious deviations will set in with local fields of the order of 100 G.
[8] We also considered true mixtures. There was no noticeable difference with the weighted averages.