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Low-temperature magnetization relaxation in magnetic molecular solids

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HIGHLIGHTS

- A novel set of non-linear rate equations for the coupled evolution of the magnetization and dipole field distribution.
- An analytic derivation of the short-time square root in time behavior of the magnetization relaxation.
- Agreement between theory and simulations without further fitting parameters.

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ABSTRACT

The low temperature relaxation of the magnetization in molecular magnetic solids such as Fe_8 is studied using Monte Carlo simulations. A set of rate equations is then developed to understand the simulations, and the results are compared. The simulations show that the magnetization of an initially saturated sample deviates as a square-root in time at short times, as observed experimentally, and this law is derived from the rate equations analytically.

1. Introduction

The low temperature relaxation of the magnetization of magnetic molecular solids such as Fe_8 has proven difficult to understand ever since the earliest experimental studies [1–3]. The time dependence of this relaxation is highly non-exponential, and fits to forms such as stretched exponentials have provided no insight even when the fits seem to be good. A second puzzling feature is that for short times, the relaxation is observed to follow a square-root behavior with time in a large number of protocols: demagnetization, magnetization, and hole-digging in which the magnetic field is abruptly changed after the magnetization has been allowed to come to an equilibrium or quasi-equilibrium

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state in response to a previous value of the applied magnetic field. A good review of the subject is given by Gatteschi, Sessoli, and Villain [4]. These authors give many more references to experimental studies [1–3,5–8], theoretical analyses [9], and Monte Carlo simulations [10,11]. Additional work is contained in Refs. [12,13].

The fundamental microscopic mechanism by which the spin of an individual molecule changes at low temperatures (say below 50 mK) is incoherent tunneling between the lowest energy states. In both Fe_8 and Mn_{12}, the anisotropy of the molecule is of the Ising type, and the lowest energy states have Zeeman quantum numbers $m = \pm S$, where S is the spin of the molecule. The tunnel splitting between these states is of order 100 Hz (in frequency units) for Fe_8 and unobservably small for Mn_{12}. It must be stressed that in the solid, the tunneling is not of the coherent flip-flop type seen in the NH_3 molecule, and previous authors have examined various decoherence processes by which the tunneling dynamics of a single molecule change from coherent to incoherent [14,15]. This is not enough to explain the observed non-exponential time behavior, for if there were a single characteristic time scale for relaxation of a single molecule, and all molecules relaxed independently, the magnetization would relax essentially exponentially in time with the same time scale as for one molecule. Thus, the non-exponential time behavior is a strong indicator that the molecules in the solid do not relax independently of each other. The biggest and most obvious coupling between molecules is the dipole–dipole interaction, and while this has been considered by many previous authors [2,9,4] a complete theory is still lacking. In particular, the $\sqrt{t}$ form has been written down by Prokofev and Stamp [9], but as noted by Gatteschi, Sessoli, and Villain [4], several aspects of their argument are unclear, and it is also unclear if the $\sqrt{t}$ form applies to all situations. These latter authors also give a heuristic argument for the $\sqrt{t}$ law for the particular case of the demagnetization problem. (We comment further or this below.) In sum, our understanding of the relaxation phenomena is incomplete and/or heuristic, and an independent analysis seems worthwhile. It is the purpose of this paper to provide one.

We note here that a rather different explanation for the $\sqrt{t}$ behavior is given by Miyashita and Saito [12]. In their approach, the magnetization relaxes entirely due to nuclear spins, which are taken to provide a field at the molecular spin site in the form of a random walk. This model has been examined in detail by Villain [13], who concludes that while it may apply to other molecular magnets under certain conditions, it cannot apply to real Fe_8, not only because the dipole field of the molecules is about 10 times larger than the nuclear spin field, but also because it is valid only if the nuclear spin relaxation is very slow. The reader is referred to Villain's paper for more details.

Our first approach to the problem is Monte Carlo simulation, as also done in Refs. [10,11]. In keeping with general practice, the detailed behavior of various microscopic features of the system are not reported in these references, so we found it necessary to do the simulation for ourselves in order to understand completely the effect of various parameters. However, Monte Carlo simulation is ultimately a form of numerical experimentation, and by itself it does not provide a physical framework for understanding of the phenomenon. We present in this paper such a framework by developing a set of rate equations for the magnetization, and the up and down spin populations on a subset of sites where the dipole field is very close to zero. These rate equations entail the distribution of dipole fields at the molecular sites. For the specific problem of demagnetization, we can construct an approximate model for this distribution, which then enables us to solve the rate equations numerically. We find that the solution to the rate equations matches the Monte Carlo results quite closely. Furthermore, we can show analytically that the solution obeys a square-root behavior with time at short times. As in Ref. [4] we have only studied the demagnetization problem. Further, the scaling behavior that we find for ancillary quantities also agrees with the heuristic argument in Ref. [4]. The additional and new features of our work over Refs. [4,9] are that we have a microscopic theory in the form of the rate equations, and the coefficient of the $\sqrt{t}$ law is *not* a fitting parameter, but is completely determined in terms of the parameters of the problem, since our model for the dipole field distributions and the rate equations requires no further ingredients or fitting parameters beyond those involved in specifying the Monte Carlo process. In this paper we focus on the problem of demagnetization of a spherical sample with a cubic lattice in order to minimize the complications from demagnetizing fields, and study the shape independent aspects of the problem, but we believe that our rate equation approach offers a method to attack a much wider class of problems, and in the future we hope to study other experimental protocols, sample shapes, and lattice types.