GIANT MAGNETOCALORIC EFFECT OF COMPRESSIBLE ISING AND HEISENBERG LATTICES

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ABSTRACT

Since the discovery of giant magnetocaloric materials, it has become clear that magnetovolume coupling can lead to a large increase to a material's magnetocaloric effect, and so, to high-performance magnetic refrigerants. A simple and computationally inexpensive approach to gauge magnetovolume effects is via the Bean-Rodbell model, where a Curie temperature dependence on volume is included in the Weiss mean-field model. The thermodynamic properties of giant magnetocaloric materials are described, namely discontinuous magnetization curves and large entropy change values. Moving to a microscopic model is a natural step to better characterize giant magnetocaloric materials. In this work we show how an Ising/Heisenberg-type interaction together with elastic/magnetovolume coupling can be solved by a Monte-Carlo method, reproducing the thermodynamic properties of giant magnetocaloric systems. The low computational cost of this approach and the possibilities of simulating systems using Density Functional Theory calculated magnetic interaction parameters allow the computational study and design of (giant) magnetocaloric materials.

Keywords: Entropy change, magnetovolume coupling, Mean-Field, Monte-Carlo simulations.
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1. INTRODUCTION

The performance of magnetic refrigeration devices depends heavily on the magnetocaloric effect (MCE) intensity of the active magnetic refrigerant. The discovery of the giant magnetocaloric effect (GMCE) [1] led to a renewed interest in this technology, now in its starting steps of commercialization following intense research in new high performance materials and devices [2]. A strong coupling between magnetic and lattice degrees of freedom is the underlying mechanism behind the GMCE, and the need for a fundamental understanding of this effect led to the use of various theoretical models. The Bean-Rodbell model [3], in particular, was successfully used in the study of several families of GMCE materials, including Gd-Si-Ge [4], Mn-Fe-P-As-Si [5,6], La-Fe-Si [7] and La-Ca-Mn-O based manganites [8], and recently on general properties of GMCE materials [9,10]. The Bean-Rodbell model consists on considering the Weiss molecular mean-field model, together with an explicit linear dependence of the Curie temperature T_C on volume:

$$T_C = T_0\left[1 + \beta\left(\frac{v - v_0}{v_0}\right)\right], \quad (1)$$

where β is a positive and constant factor of proportionality, v volume, v_0 equilibrium volume in the absence of magnetic interactions and T_0 the Curie temperature for $v = v_0$. For a given magnetic system with K compressibility, the η parameter is defined as:

$$\eta = 40\, Nk_B KT_0\beta^2 \frac{\left(S\left(S+1\right)\right)^2}{\left(2S+1\right)^4 - 1}, \quad (2)$$

where S is spin, N the spin density and k_B the Boltzmann constant. For $0 < \eta \leq 1$ the paramagnetic (PM) to ferromagnetic (FM) transition is of the second-order, while for $\eta > 1$ it is of the first-order, increasing the isothermal magnetic entropy change ΔS_M, particularly near T_C.

The popularity and usefulness of the Bean-Rodbell model is due to its semi-quantitative validation of the overall thermodynamic properties of a GMCE material, and also to its simplicity and low computational cost. For reference, Bean-Rodbell model simulations of thousands of *M(H,T)* data points of a GMCE system typically take minutes to run in a standard personal computer using available software packages, such as the Mean Field Simulation Suite (MFSS) [11]. Still, the correlation between the microscopic properties of a given MCE material (atomic types, structure) is difficult to gauge in a mean-field approximation. Typically, an average spin value is used, and the remaining model parameters values, T_0 and η, are chosen to replicate experimental results. In short, it is possible to interpret experimental magnetic and magnetocaloric properties of a given GMCE material, but difficult to predict them using a mean-field model.

A microscopic approach would allow a more realistic description of GMCE materials, provided the thermodynamics of the first-order phase transition are adequately described. A predictive approach to magnetocaloric performance could also be envisaged, as microscopic parameters can be estimated by well-established Density Functional Theory (DFT) methods. To our knowledge, there are few quantitative combined DFT + Monte-Carlo (MC) approaches to study MCE materials. A mixed-valence rigid Heisenberg lattice study of La-Ca-Mn-O manganites [12], with previously calculated *J* values [13] has led to comparable results with experiment, albeit considering no magnetovolume coupling, which is known to be relevant in this system [14]. Co and In doped Ni-Mn-Ga shape memory alloys were studied via the use of a Potts Hamiltonian with $2S + 1$ possible spin projections, in accordance with the total spin of each magnetic atom, and the three-state Blume-Emery-Griffiths model, which allows for a structural transformation from the cubic (austenitic) phase to the tetragonal (martensitic) phase [15]. The magnetocoupling interaction was taken into account via two parameters with values chosen in order to reproduce the experimental martensitic transformation temperature and magnetization behavior in different magnetic fields. Simulated results compared qualitatively well with experiment.

A more widespread use of microscopic models in the study of MCE materials would be achieved by overcoming two main hurdles: the complexity of the models usually employed and the computational costs of calculations. In this work we propose an Hamiltonian, following the ideas of Domb [16], which follows essentially the same assumptions as the Bean-Rodbell model (section 2). Calculations of relevant thermodynamic properties are performed via the use of a MC method (section 3), that drastically reduces computational costs of simulating *M(H,T)* data, when compared to the more widely used Metropolis [17] algorithm.

2. MAGNETOVOLUME COUPLING MODEL

For a simplified description of magnetovolume interactions, we start with a typical Ising/Heisenberg interaction, where the magnetic interaction between neighboring spins depends on their interatomic distance, a volume energy potential and interaction with external field:

$$\mathrm{H} = -\frac{1}{2}\sum_{<i,j>}\left[J(v)S_i \cdot S_j\right] + \frac{1}{2}Kv^2 - MH \quad , \tag{3}$$

where J is the magnetic exchange parameter between S_i and S_j spins, K compressibility, M magnetization and H applied magnetic field. For a direct comparison with Bean-Rodbell model calculations, we here assume that the $J(v)$ dependence is linear, with positive slope. Explicitly, $J(v)=J\_o+J'(v-v_0)/v_0$, where J_0 is the magnetic exchange parameter for $v = v_0$ and J' a positive constant. Fig 1 illustrates the energy potentials in play:

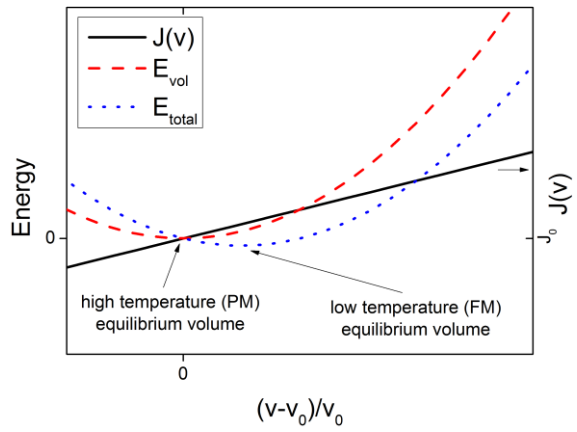

Figure 1. Energy potentials of eq. 3: magnetic exchange parameter dependence on volume (solid line), volume energy potential (dashed line) and total volume and magnetic energy potential (dotted line).

In the PM state, the system will tend to be near its structural energy minimum ($v \sim v_0$), as magnetic energy will be low. In contrast, the FM state will energetically favor a volume $v > v_0$, as the magnetic energy contribution is strong and it becomes favorable for the system to have a higher J value, and consequently a larger v value. In analogy to the Bean-Rodbell model, for a sufficiently high magnetovolume coupling, the system should discontinuously change M and v at T_C. While solving the Ising/Heisenberg model Hamiltonian with standard MC methods such as the Metropolis algorithm is now relatively straightforward, its computational cost is considerable. Each $M(H,T)$ data point requires a converged calculation. Also, data for $T \sim T_C$, which is in the area of interest for MCE materials, requires longer convergence times, or the use of more complex approaches (e. g. cluster models [18-20]) to avoid noise due to critical slowing down.

By introducing the magnetovolume term, the use of Metropolis method becomes more computationally expensive. Both v and M parameters will require adequate convergence, which will not happen without the introduction of an extra pressure term [21]. To avoid the use of this term, and also to reduce the overall computational needs for the required data simulations, we propose the use of MC methods that determine the Joint Density of States (JDOS), such as the Wang-Landau [22], transition matrix [23] and Random Path Sampling (RPS) [24] methods. From (J,H,T)-independent JDOS calculations, which are done only once for each lattice type, all relevant (J,H,T)-dependent thermodynamic quantities are obtained from either the partition function or free energy minima. In terms of computational cost, this is a much more favorable approach compared to individual M(H,T,J) converged calculations as required by the Metropolis method. Due to its simple implementation and parallelization, we here employ the RPS method for JDOS calculations. The methodology and implementation is briefly discussed in the next section.

3. MONTE-CARLO METHOD

For obtaining a reliable JDOS estimate of a system with a large number of possible Energy-Magnetization states, an efficient statistical sampling of these states is required. A simple approach is the RPS method which, by construction, results in unbiased, flat M sampling by sweeping from the -1 total M to the +1 total M configuration via locally flipping spins from the -1 to the +1 state, from a random sequence. Energy values are evaluated locally, much like in the Metropolis method, ensuring a fast update of total energy value. Each complete RPS sweep corresponds to flipping all spins in the lattice. Depending on model type and system size, for a number of sweeps that is orders of magnitude below the total number of possible states, converged estimates of JDOS (and consequently of the partition function and free energy) are achieved. For discrete spin models, such as the Ising model, the implementation is straightforward, while for continuous spin model (Heisenberg) we here approximate the continuous spin direction degree of freedom to 14 total vector directions, which is larger than the minimum of 12 shown to be able to describe the critical behavior of the model [25]. Convergence of JDOS calculations is evaluated by the overall smoothness of free energy $F(H,T)$ at zero field, particularly for $T \sim T_C$. Data points shown in this work are taken from the absolute F minimum.

4. RESULTS

We compare the mean-field Bean-Rodbell model simulations of second- and first-order FM-PM transitions, from changing η values from 0 up to 2, while in the case of Ising and Heisenberg model, the J dependence on volume slope changes from 0 to 3.5, considering a K value of 50. Fig. 2 (left) shows the zero-field M vs T behavior of the Bean-Rodbell model and a 128 spin compressible BCC Ising lattice.

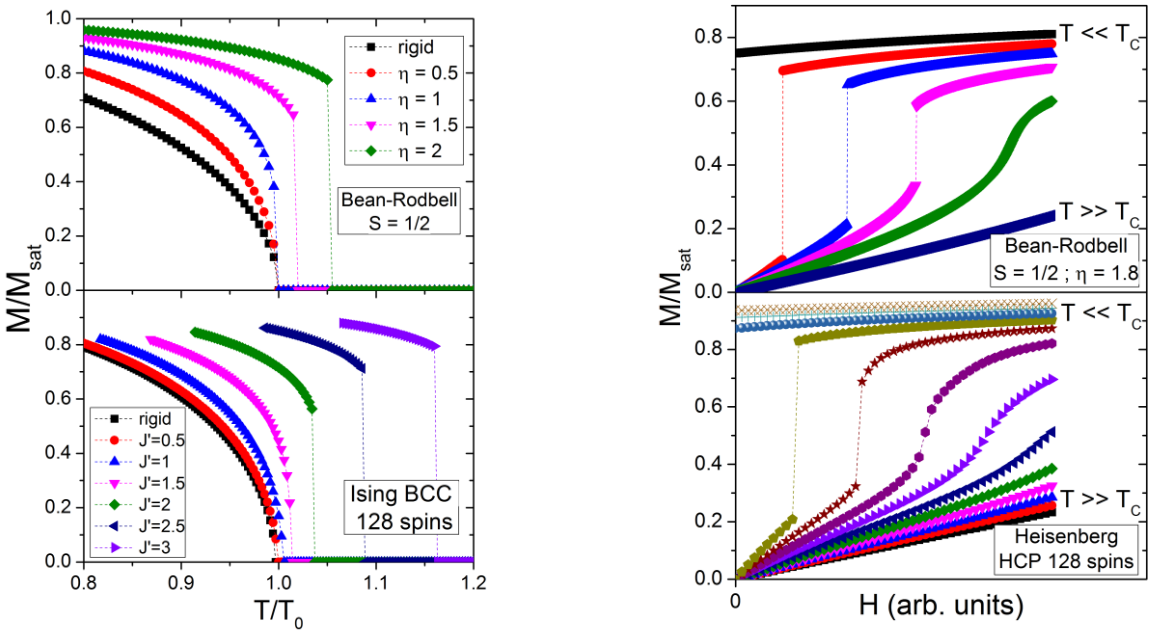

Figure 2. (left) Spontaneous magnetization and (right) isothermal magnetization calculations of Bean-Rodbell (top) and microscopic (bottom) models, for rigid and compressible systems with increasing magnetovolume coupling. Dashed lines are eye-guides.

Both the Bean-Rodbell and compressible Ising systems show qualitatively the same behavior, in terms of the transition becoming first-order for sufficiently high magnetovolume coupling, as seen through the increase in T_C and the discontinuity of the M vs. T curve. In terms of isothermal M versus H behavior, for sufficiently high magnetovolume coupling, the Bean-Rodbell model shows metamagnetic-like behavior (inflexions in $M(H)$) and for stronger magnetovolume coupling, discontinuities up to a certain critical field. Fig. 2 (right) shows the $M(H)$ dependence of a first-order Bean-Rodbell system, together with a compressible HCP Heisenberg system.

The metamagnetic-like isothermal M vs. H behavior of the Bean-Rodbell model is also qualitatively reproduced by the compressible Heisenberg model, following the Hamiltonian of eq. 3. Taking into account the two previous results, we should also see a large increase in the MCE when comparing rigid and compressible lattices. Fig. 3 compares the isothermal entropy change of Bean-Rodbell and compressible HCP Heisenberg systems.

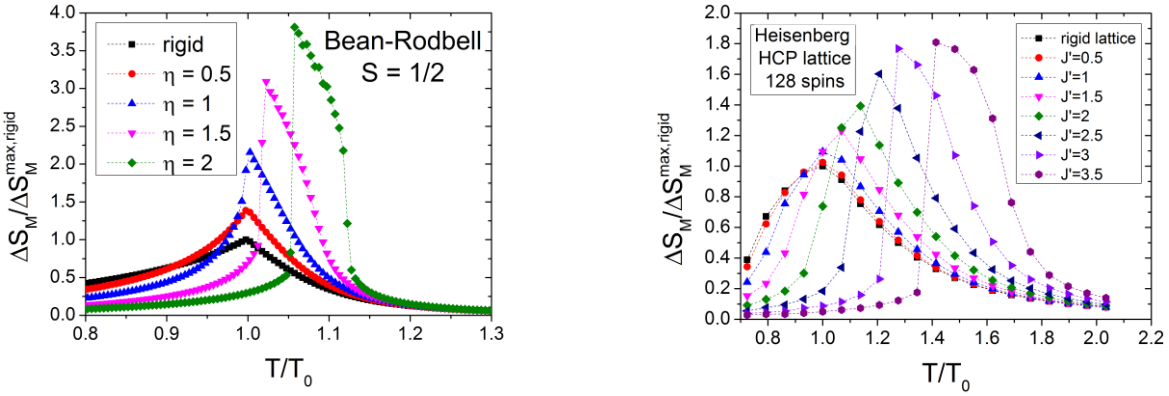

Figure 3. Isothermal magnetic entropy change ΔS_M vs T of Bean-Rodbell (left) and HCP Heisenberg (right) models, for rigid and compressible systems with increasing magnetovolume coupling. Dashed lines are eye-guides.

The same overall thermodynamic behavior is observed between the two models, with similar increases in entropy change and changes in the curve shape with increasing magnetovolume coupling. The necessary ingredients to study GMCE materials are present in the Hamiltonian of Eq. 3.

5. COMPUTATIONAL COSTS

As stated previously, a more widespread use of combined DFT and MC approaches for MCE materials studies will benefit from low computational cost of simulations. By using JDOS-based methodologies, such as the RPS method here employed, the bulk of intensive calculations are done for obtaining JDOS itself. In this work, we used previously calculated JDOS for all Ising and Heisenberg lattices here under study. The data shown on Figs. 2 and 3 took minutes to simulate using a standard personal computer. Other (H,T)-dependent thermodynamic properties, such as free energy and volume were also calculated. The Bean-Rodbell simulations here shown, performed using the freely available MFSS software, took a comparable amount of time to be performed. For a combined DFT and MC approach, the computational time required for DFT calculations of magnetic interaction J parameters is naturally relevant, and will depend on the DFT package used. Nonetheless, both the SPR-KRR [26] and openmx [27] packages, which employ the Liechtenstein method for J value calculations [28], are sufficiently fast for systematic calculations in various structures and compositions, as recently explored [15].

6. CONCLUSIONS

We have here proposed a simple Hamiltonian, that includes a magnetic interaction between spins together with a lattice potential and volume-dependent magnetic coupling. Through Monte-Carlo computations of the joint density of states of Ising and Heisenberg lattices, magnetic and magnetocaloric properties were simulated with increasing magnetovolume coupling strengths and compared to simulations of the widely used Bean-Rodbell mean-field model. We have found that the overall thermodynamics of first-order phase transitions are represented in the model here proposed, making it applicable to the study of giant magnetocaloric materials. The low computational cost of the calculations here performed is relevant for widespread use, while a proposed combination with density functional theory can provide the basis for predictive computational materials design of high-performance magnetic refrigerants.

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