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Temperature- and field-induced entropy changes in nanomagnets

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Room-temperature magnetic-entropy changes in nanostructures for magnetic refrigeration are investigated by model calculations. Using a mean-field approach, the magnetic entropy is calculated as a function of temperature, magnetic field, particle size, anisotropy, and interaction strength. Both isotropic (Heisenberg) and uniaxial (Ising and *XY*) anisotropies are considered. The nanoparticle entropy strongly depends on the character of the anisotropy, in contrast to atomic ferromagnetism, where the anisotropy energy is much smaller than the interaction energy. Most promising are isotropic particles and particles with weak easy axis anisotropy, as well as easy-plane particle with the field in the plane. The optimum nanoparticle size is not much larger than 1 nm, because the relative magnetization direction in a nanoparticle is usually frozen and do not contribute to the entropy change. © *2008 American Institute of Physics*. [DOI: 10.1063/1.2835094]

Magnetic refrigeration is an energy-efficient and environment-friendly technology. First, magnetic refrigeration does not use ozone-depleting chemicals and is therefore environmentally friendly. Second, the cooling efficiency is better than that of gas-compression refrigeration. For many decades, a similar idea has been applied in low temperature physics, in the adiabatic demagnetization of paramagnetic salts, but advanced research focuses on magnetic refrigeration at room temperature.[1–3] Present-day magnetic cooling relies on atomic degrees of freedom, such as the spin orientation of Gd 4*f* shells in magnetic compounds. Most fundamental and applied research has focused on bulk materials such as $Gd_3Ge_2Si_2$,[1,2] which can be produced in large amounts. However, the number of suitable compounds is limited. Almost all materials show some magnetocaloric effect, but the entropy gain is typically small and appreciable only in inconvenient field and temperature regions. Nanostructures are far more flexible with respect to the optimization of material properties, including magnetocaloric effects.[3–5] One advantage is that the magnetization of suitable nanostructures can be switched by an applied magnetic field of the order one 1 T (10 kOe) or less, which are easily realized by using permanent magnets such as $Nd_2Fe_{14}B$ and do not require superconducting magnets.[6,7]

The idea behind magnetic cooling is to exploit entropy changes in spin systems. The starting point is the free energy

$$F = U - TS - \mu_0 \int \mathbf{M} \cdot \mathbf{H} dV, \qquad (1)$$

where *U* is the internal energy, *T* is the temperature, *M* is the magnetization, and *H* is the magnetic field. The entropy exploited in magnetic cooling originates from the relative orientation of the atomic magnetic moments, meaning that a field changes the entropy *S* and, via *M* and *TS*, the temperature. While a magnetic field aligns the spin and thereby re-

duces the entropy, only a part of Zeeman energy $\mu_0 \int \mathbf{M} \cdot \mathbf{H} dV$ enters the magnetic entropy balance. Let us consider nanoparticles containing *N* spins of moment μ_B (spin 1/2), or N/S_{at} atoms, where S_{at} is the number of spins per atom ($S_{at} = 7/2$ for Gd^{3+}). Figure 1 compares the Curie transition (a) with a Stoner-Wohlfarth-type micromagnetic magnetization rotation (b), as typically encountered in small particles. Furthermore, one must keep in mind that magnetization changes in nanostructures are often micromagnetic, that is, unrelated to thermal fluctuations and not accompanied by entropy changes (Fig. 2). The focus of this paper is on the magnetic entropy of noninteracting nanoparticles and of nanoparticles coupled by exchange interactions, with particular emphasis on anisotropy and particle-size dependence.

The equilibrium entropy is calculated from the partition function $Z = \Sigma_i \exp(-E_i/k_B T)$, where the summation includes all states that are actually accessed during a typical experi-
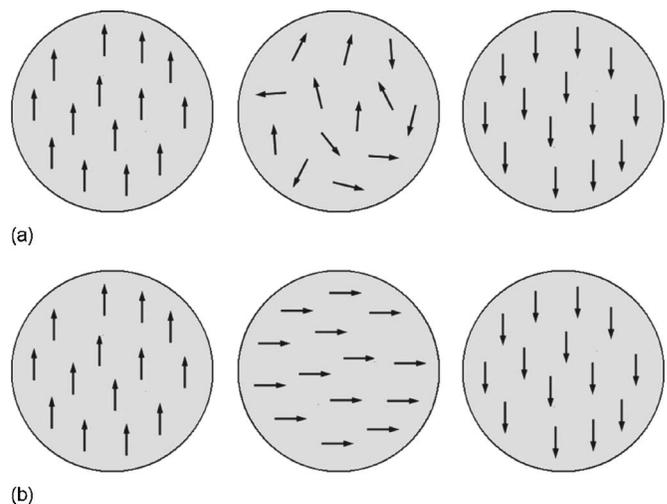

(a)

(b)

FIG. 1. Magnetization changes in a nanoparticle: (a) phase transition and (b) magnetization reversal. The change is usually of the type (b), meaning that the relative spin orientation inside the particle is frozen and does not contribute to the entropy change. Each arrow represents an atomic spin.

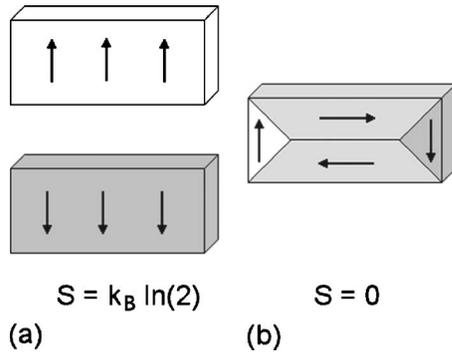a)Electronic mail: rskomski@neb.rr.com.

FIG. 2. Realization of states with zero net magnetization: (a) thermodynamic fluctuations and (b) micromagnetic regime.

ment or application cycle. In other words, equilibrium thermodynamics requires ergodicity, but relative magnetization directions are often frozen in magnetic nanostructures and thermodynamic equilibrium is usually limited to length scales of less than about 1 nm.[7,8] A similar situation is encountered in mechanical glasses, which are nonergodic because ensemble averages (liquidlike snapshots of pieces of glass) differ from time averages (solidlike frozen atomic configurations).[9]

Thermal averages are obtained from the well-known relation $\langle A \rangle = \Sigma_i p_i A_i$, where $p_i = \exp(-E_i/k_BT)/Z$ is the probability of encountering the ith state. This includes the expression $S = -k_B \Sigma_i p_i \ln(p_i)$ for the entropy. Free isotropic particles, as well as isotropic particles interacting in the mean-field approximation, obey $E_i = -\mu_0 \mu_B H s_{zi}$, so that S becomes a function of the magnetization. Furthermore, the entropy of nanoparticles exhibits a pronounced dependence on the magnetic anisotropy. This is in contrast to atomic ferromagnetism, where the anisotropy (less than 1 K per atom) is much smaller than the exchange (more than 100 K per atom) and important only in the vicinity of T_C. Nanoparticle anisotropy energies roughly scale as $N \sim R^3$ and are often larger than the interparticle interaction.

In the following, we will describe our magnet by the quasiclassical mean-field Hamiltonian,

$$H = -NJ_{eff}m\langle m \rangle - NK_u m^2 - N\mu_0\mu_B Hm, \tag{2}$$

where K_u is the uniaxial anisotropy per spin,[6,8] m is a dimensionless and normalized magnetization variable, and the exchange J_{eff} describes the interaction between the particles. Dipolar interactions require more elaborate mean-field Hamiltonians, because they may lead to the formation of columnar structures, but otherwise they affect the entropy in a manner similar to exchange.

Let us first neglect the interaction and compare isotropic magnets with uniaxial magnets of anisotropy constant K_u (both easy axis and easy plane). There are two well-known and rather trivial high-temperature limits, namely, isotropic particles ($K_u=0$) and Ising magnets ($K_u=\infty$). Isotropic particles have $2N+1$ Zeeman-split states and $S = k_B \ln(2N+1)$, or $S = k_B \ln(2N)$ in the approximation of Eq. (2), whereas Ising magnetism corresponds to two states ↑ and ↓ with equal probability and $S = k_B \ln(2)$. For arbitrary fields and temperatures, the free energy

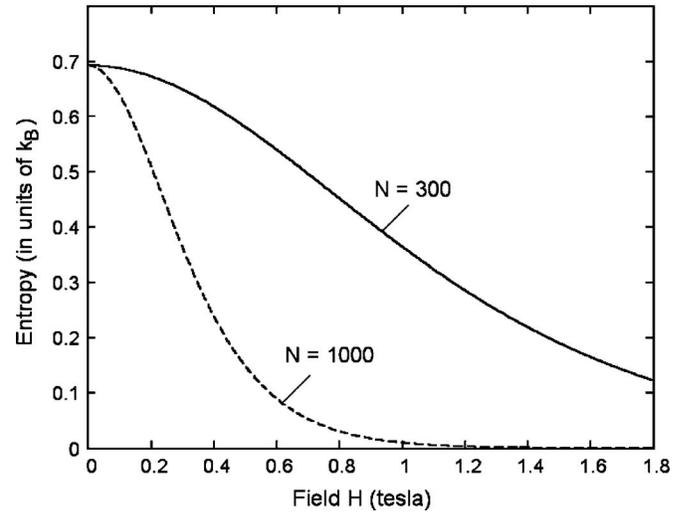FIG. 3. Entropy of Ising spin clusters.

$$F = -k_BT \ln \left(2 \cosh \frac{\mu_B NH}{k_BT} \right) \tag{3}$$

of an Ising spin yields the well-known equation of state $M = \mu_B \tanh(\mu_B NH/k_BT)$ and the entropy

$$S = k_B \ln \left(2 \cosh \frac{\mu_B NH}{k_BT} \right) - \frac{\mu_B NH}{T} \tanh \frac{\mu_B NH}{k_BT}. \tag{4}$$

This entropy decreases from $S = k_B \ln 2 - \mu_B^2 N^2 H^2 / 2k_B T^2$ in small fields to $S=0$ in large fields. Fig. 3 shows the room-temperature entropy for two particle sizes.

The calculation of the partition function for intermediate anisotropy[8] requires some bookkeeping but is straightforward. Figure 4 shows the room-temperature entropy of noninteracting particles as a function of the anisotropy field $H_a = 2K_u V_{at}/\mu_0\mu_B$, where V_{at} is the volume per spin. Fields between 0 and about 1 T are easily created by permanent magnets, and the corresponding entropy gain corresponds to gray area in Fig. 2. We see that isotropic magnets ($H_a=0$) and
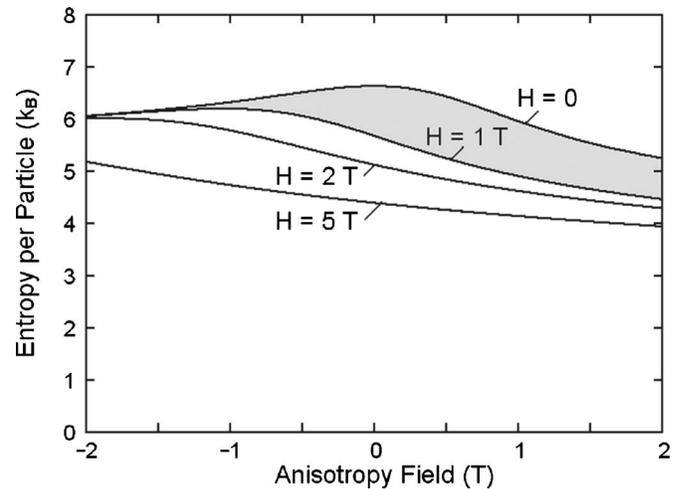

FIG. 4. Field-dependent room-temperature entropy of nanoparticles containing 1000 atomic spins. Negative, zero, and positive anisotropy fields correspond to easy-plane anisotropy, isotropic magnetism, and easy-axis magnetism. The gray area is the field range easily created in permanent-magnet systems.
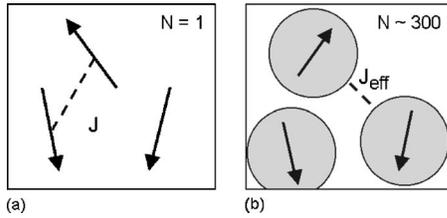
FIG. 5. Microscopic origin of the entropy change responsible for magnetic cooling: (a) atomic spins in solid and (b) interacting nanoparticles.

FIG. 7. Temperature dependence of the entropy of nanoparticles having 1000 spins, a net interparticle exchange of 1150 K, and an anisotropy field of 0.1 T. Magnetic cooling exploits the gray area.

magnets with weak easy-axis anisotropy ($H_a > 0$) yield the largest entropy changes. Easy-plane anisotropy ($H_a < 0$) makes the entropy nearly independent of the field component parallel to the anisotropy axis, because the magnetization is largely confined to the basal plane. However, in-plane fields can be shown to yield appreciable entropies.

As in atomically structured magnets, interactions (J_{eff}) are potentially helpful to enhance the entropy differences (Fig. 5). The mean-field entropy is obtained by adding the corresponding J_{eff} term to H in Eq. (4). Figure 6 compares the entropy of interacting and noninteracting particles. The effect is maximized when the interaction strength J_{eff}/k_B is close to room temperature, as assumed for the solid line in Fig. 6. Very small interactions do not yield an appreciable effect, whereas very strong coupling assimilates the system's behavior to macroscopic bulk magnets. However, the fine-tuning of the interaction is not very critical, because the maximum of the entropy density change is very broad. In small fields, the entropy change for the interacting nanoparticles ($J_{eff} = k_B T$) is $\frac{3}{4} (\mu_0 \mu_B H / k_B T)^{4/3} N^{1/3}$, as compared to the term $\frac{1}{2} (\mu_0 \mu_B H / k_B T)^2 N$ briefly discussed below Eq. (4).

The maximum entropy of a particle containing N atoms of spin $1/2$ is $\ln(2N)$, so that the entropy *per atom* is $\ln(2N)/N$. This entropy scales as $1/N$, and there is no point

in using very large particles. Similar entropy dependences are obtained for other spin models. Since $\mu_B/k_B = 0.672$ K/T, a few hundred spins are sufficient for room-temperature fields of order 1 T (Fig. 7), and smaller numbers are achievable by exploiting interactions. We actually promote a hybrid technology intermediate between atomic-scale and nanoscale cooling, combining the benefits of both approaches. Possible practical realizations are embedded nanoparticles weakly interacting through RKKY-type exchange[10,11] and multilayered magnets with competing ferro- and antiferromagnetic interactions.[12]

In conclusion, we have investigated the entropy gain and magnetic-cooling capabilities of nanostructures for magnetic refrigeration. Nanostructuring improves the entropy change in low fields and at high temperatures but yields some reduction in the maximum entropy change per atom due to frozen magnetization directions in the nanoparticle. An important feature of magnetic nanoparticles is that the entropy exhibits a strong dependence on the magnetic anisotropy. This can be exploited for magnetic cooling.
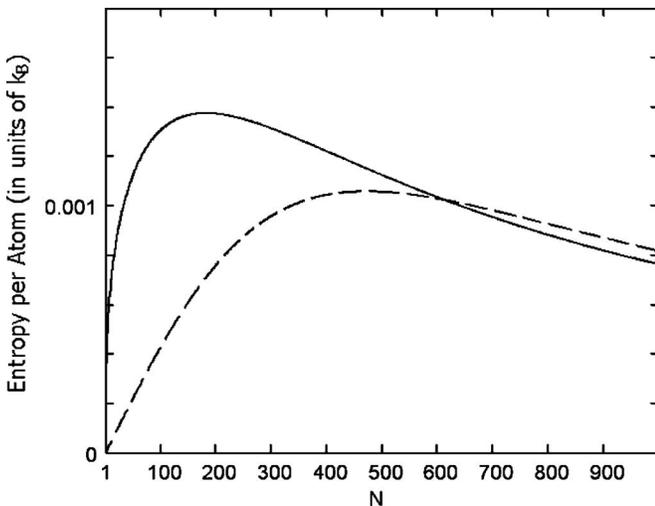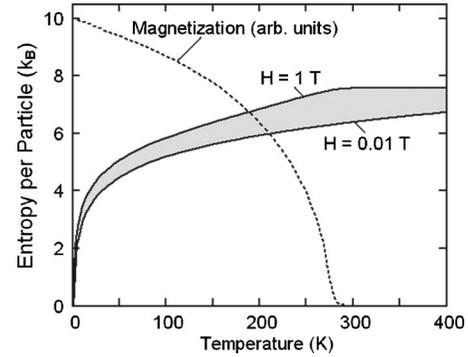
FIG. 6. Room-temperature entropy gain per atom: interacting particles (solid line) and noninteracting particles (dashed line) in a field of 1 T. The interaction is treated on a mean-field level and adjusted to maximize the effect near room temperature.

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