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# Magnetocaloric effects in magnetic nanoparticle systems: A Monte Carlo study

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**Abstract**

A superparamagnetic nanoparticle system is a good candidate for implementing the magnetocaloric effect, due to its suitable properties as a frozen ferrofluid able to follow a thermodynamic cycle. For such aim, we have concentrated on the study of the entropy dependence on both the particle size and sample concentration using a Monte Carlo simulation. We have found that for a given sample concentration there exists a particle size for the larger entropy increase, and reciprocally for a given particle volume there exists a sample concentration able to produce the larger entropy change.


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*Keywords:* Monte Carlo simulations; Nanoparticles

## 1. Introduction

The magnetic properties of a superparamagnetic system depend both on the particle size and the interparticle distances. In the limit of weak interactions an increase in the blocking temperature with particle density has been obtained in some experiments [1,2]. Numerical simulations [3] were made for explaining the above physical behavior using a basic nanoparticle model where the energy terms are: anisotropy energy, field energy and dipolar interaction energy. Unfortunately it seems that this issue has still an amount of controversy in the literature [4] due to the complexity of the phenomena involved. For this sake we present in this paper some preliminary results using a modification of the Monte Carlo implementation mentioned in Ref. [3]. We simulate the particle size dependence of the magnetization for a fixed number of particles for a zero field cooling curve (ZFC) conditions. In a complementary form we introduce also the magnetization yielded by changing the sample concentration of particles with a fixed mean volume. In both cases the entropy is calculated and evaluated for its contribution to the study of the magnetocaloric effect.

## 2. Monte Carlo simulation conditions

The physical model employed for our numerical simulations is the same as in Ref. [3], where the particle sample is a ferrofluid without aggregations where the positions of the particles are kept fixed and the easy axes are chosen randomly. The energy of each particle is considered to have three main sources: anisotropy ($E_{\mathrm{A}}$), Zeeman ($E_{\mathrm{H}}$) and dipolar interaction ($E_{\mathrm{D}}$).

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In the superparamagnetic model it is assumed that single domain magnetic particles with inner coherent magnetization rotation of the atomic moments, result in a total particle magnetic moment of constant absolute value $|\vec{\mu}_i| = M_S V_i$, where $M_S$ is the saturation magnetization, considered to be independent of the particle volume $V_i$. According to Ref. [3] we consider a monodisperse assembly due to its moderate importance in our present problem. This theoretical prediction is borne out by recent experimental works [2].

The computational treatment of the energy is the same as in Ref. [3], where the particles are placed in a liquid-like arrangement with periodic boundary conditions. The Metropolis algorithm is applied over all the particles repeating the process until the magnetization of the system reaches a stability criterion.

The parameters varied in our simulation are the sample concentration $N$ and the volume of the particles $V$, which is varied by means of the related parameter $R = V/L^3 c_0$, where $L$ is the edge of the cubic simulation box and $c_0$ is a unitless constant characteristic of the material. The unit cubic cell remains constant over all the simulations.

## 3. Results and discussion

In Fig. 1 are represented the ZFC curves for different particle volumes for $N = 64$.

The observed displacement of the ZFC curve maximum as the particle volume is increased reflects the superparamagnetic character of the system: the blocking temperature ($T_B$) linearly increases with increasing particle size [5] as shown in the inset.

In order to obtain the magnetocaloric effect we calculate the corresponding entropy. By the usual Maxwell's thermodynamics relation [6] for a discrete magnetic field and temperature variation, the entropy evolves approximately as a discrete summation [7], which converted to our reduced magnitudes results in

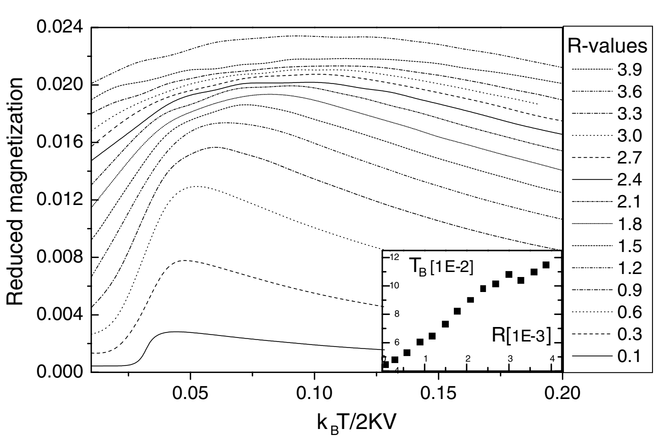


Fig. 1. Reduced magnetization versus the reduced temperature for different particle volumes ($R$ [Exp(−3)]).

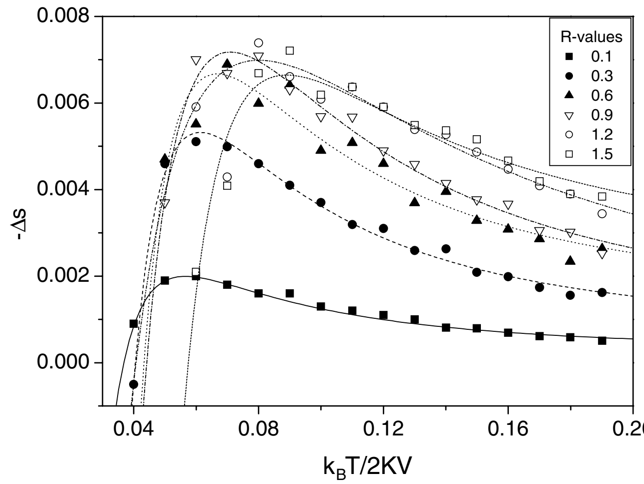


Fig. 2. Negative entropy change plotted against the reduced temperature for different values of $R$ [Exp(−3)].

$$\Delta s = \frac{m(\beta_{i+1}^{-1}, h) - m(\beta_i^{-1}, h)}{\beta_{i+1}^{-1} - \beta_i^{-1}} \Delta h, \tag{1}$$

where $m = R\sum_i \cos\theta_i$ is the reduced magnetization, $\beta$ is the inverse of the reduced temperature and $s$ is the resulting reduced entropy. In Fig. 2 the dependence on the particle volume of the negative entropy change is plotted for temperatures above $T_B$, where the computational results were fitted to a Langevin-like function. The maximum enhancement is observed to occur for $R = 0.0009$. It is also observed that the entropy maximum undergoes a temperature increase as the volume does, in accordance with the blocking behaviour from Fig. 1.

In Fig. 3 the negative entropy change associated to different sample concentrations $N = 8$, 27, 64 and 125 for a fixed particle volume ($R = 0.0010$), is calculated from the corresponding ZFC curves. It is observed that the maximum entropy enhancement correspond to the value

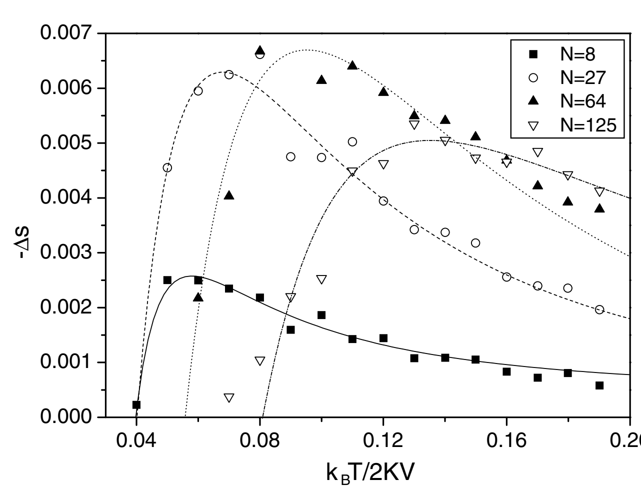


Fig. 3. Negative entropy change in function of the reduced temperature for different sample concentrations ($N$).

$N = 64$, reflecting the fact that there exists a sample concentration which results in a larger entropy increase.

## 4. Conclusions

For the magnetocaloric effect implementation the properties of a superparamagnetic nanoparticle system are influenced both by the particle size and the sample concentration. Above the blocking temperature it is possible to fit the particle size-sample concentration conditions for a larger negative entropy increase, which we simulated by means of a Monte Carlo technique.

The entropies associated to these physical processes are quite small, this suggests that for a practical application for the magnetocaloric effect it would be necessary to search for different sources. A good candidate for such a condition could stand below the blocking temperature, because the much higher slope of the magnetization curves. Unfortunately this region strongly depends on the dynamics of the system and much care has to be done for avoiding unreal results.

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