Eur. Phys. J. B **19**, 117–119 (2001)

THE EUROPEAN PHYSICAL JOURNAL B

EDP Sciences

Paradoxical magnetic cooling in a structural transition model

P. Borrmann[1], H. Stamerjohanns[1,a], E.R. Hilf[1], and D. Tománek[2]

[1] Department of Physics, Carl von Ossietzky University, 26111 Oldenburg, Germany
[2] Department of Physics and Astronomy, Michigan State University, East Lansing, Michigan 48824-1116, USA

Received 5 September 2000

Abstract. In contrast to the experimentally widely used isentropic demagnetization process for cooling to ultra-low temperatures we examine a particular classical model system that does not cool, but rather heats up with isentropic demagnetization. This system consists of several magnetite particles in a colloidal suspension, and shows the uncommon behavior of disordering structurally while ordering magnetically in an increasing magnetic field. For a six-particle system, we report an uncommon structural transition from a ring to a chain as a function of magnetic field and temperature.

PACS. 05.70.Fh Phase transitions: general studies – 75.10.-b General theory and models of magnetic ordering – 75.50.Mm Magnetic liquids

1 Introduction

Cooling to ultra-low temperatures is presently experimentally achieved using the isentropic demagnetization process suggested in 1926 by Debye and Giauque [1,2]. Here we study the thermal and magnetic properties of a particular model system consisting of six magnetite nanoparticles in a colloidal suspension. Our calculations indicate that changing the temperature or magnetic field leads to a transition from a ring-like to a chain-like structure. We demonstrate that such a model system, that could be realized in a ferrofluid, would not cool but rather heat up during an isentropic demagnetization. The system of magnetic nanoparticles shows the uncommon behavior of disordering structurally, *i.e.* increasing its volume in phase space, while ordering magnetically in an increasing magnetic field. This behavior, associated with the break-up of the relatively rigid rings to floppy chains, occurs once the energy gain upon aligning a chain of dipoles with the field exceeds the energy cost of breaking up a ring. Thus systems that disorder structurally in high fields may be used as coolants based on isentropic magnetization instead of demagnetization. So far, only ferrofluid systems with a large number of particles have been discussed as candidates for use in magneto-caloric heat engines [3]. Here we report a paradoxical magnetic cooling phenomenon that is unique to systems with only few particles.

Both the conventional and paradoxical process utilize the energy change associated with particular structural changes for cooling. The *conventional* isentropic demagnetization process uses the fact that a magnetic system, such as a spin system, orders magnetically and thus lowers its entropy in presence of an external magnetic field. Removal of the external magnetic field at constant temperature leads to an increase in entropy due to magnetic disordering, which requires energy. Decreasing the external magnetic field at constant entropy consequently leads to a temperature lowering. With this method, systems such as copper have been cooled down to temperatures as low as 50 nK [4].

In the following we address model systems consisting of a finite number of magnetic particles that may undergo structural transitions. Both the structural and magnetic degrees of freedom are important in this system and can not be decoupled. Applying a sufficiently high magnetic field causes the system to order magnetically while disordering structurally, at the cost of internal energy. Consequently, such a system will exhibit the paradoxical phenomenon of cooling by isentropic magnetization.

The transformation from a ring to a chain is associated with freeing up a structural degree of freedom, with a corresponding increase in entropy. Such a transformation can be induced by a magnetic field in a system of magnetic dipoles, where the energetics is governed by dipole-dipole interactions between the particles and an interaction of each particle with the external field. In small fields, the ring is stabilized with respect to the chain structure if the gain in dipole-dipole interaction upon connecting the chain ends energetically outweighs the dipole misalignment energy in a bent structure. The energy gain upon aligning all individual dipoles with a sufficiently high applied field, on the other hand, stabilizes the chain structure.

One system that satisfies all the requirements on a paradoxical magnetic coolant consists of a few ($4 \leq N \leq 14$) super-paramagnetic particles of magnetite. Such particles are the key constituents of ferrofluids, which

[a] e-mail: stamer@uni-oldenburg.de

have attained rapidly increasing interest during the past few years [5,6]. Recently we have shown that such systems exhibit intriguing phase transitions between the ordered ring and chain phases and one disordered phase [7]. We also pointed out that self-assembly in these systems could be used to store information [8].

2 The model

In the following, we study the thermodynamic behavior of a six-particle system, where the chain and the ring are the dominant stable structural isomers. We chose this particular system as it allows a simple discussion of the two thermodynamical features characteristic of isomer transitions in finite systems, namely the isomeric phase space and the transition probability that is linked to the transition time. It is true that such ring and chain isomers are also stable at much larger sizes. Nevertheless, the thermodynamical behavior becomes more complex in larger systems, where the number of relevant structural isomers grows rapidly with increasing N.

Here we calculate the entropy and the dependence of temperature on an external magnetic field at constant entropy $(\partial T/\partial B)_S$ for a model system of six magnetite particles with a radius $\sigma = 50$ Å and a permanent magnetic moment of $\mu = 2.63 \times 10^3\ \mu_\mathrm{B}$. The total potential energy U of this system is given by [6]

$$U = \sum_{i<j}^{N} \left\{ (\mu_0^2/r_{ij}^3) \left[\hat{\mu}_i \hat{\mu}_j - 3(\hat{\mu}_i \hat{r}_{ij})(\hat{\mu}_j \hat{r}_{ij}) \right] + \epsilon \left[\mathrm{e}^{\left(-\frac{r_{ij}-\sigma}{\rho}\right)} - \mathrm{e}^{\left(-\frac{r_{ij}-\sigma}{2\rho}\right)} \right] \right\} + \sum_{i=1}^{N} \mu_z^i B_\mathrm{ext}. \quad (1)$$

The pairwise interaction energy is given by the dipole-dipole and a non-magnetic interaction energy. The latter is dominated by a repulsion between the spherical particles, but contains also a weak attractive part due the van der Waals interaction. It is modelled by the above Morse-type potential with parameters [10] $\epsilon = 15.1\ \mu$eV and $\rho = 2.5$ Å. The second sum reflects the interaction between the magnetite particles and the external magnetic field B_ext that is aligned with the z-axis.

We would like to point out that the finite ferrofluid systems undergo all the intriguing transitions described below occur independent of these parameter values. Our particular choice has been taken to bring the transition into an experimentally accessible and interesting region [9].

All thermodynamic quantities can be derived from the canonical partition function $Z(B,T)$ by appropriate differentiation. We determined Z using the Metropolis Monte Carlo method [11], which we combined with a special type of optimized data analysis [12] to calculate all thermodynamic properties as functions of the temperature T and the magnetic field B_ext as external variables [7]. The entropy S is given by

$$S = k_\mathrm{B} \left(\ln(Z) - \beta \frac{\partial \ln(Z)}{\partial \beta} \right), \quad (2)$$

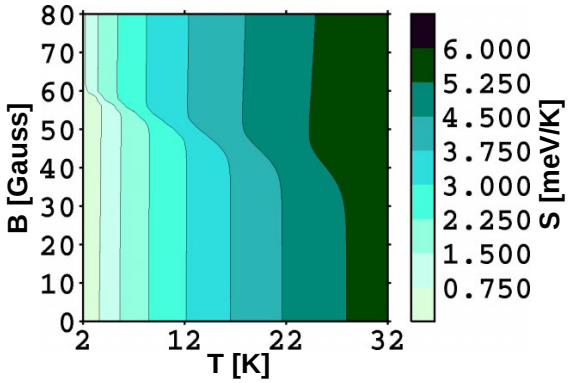

Fig. 1. Contour plot of the entropy S as a function of the external magnetic field B_ext and temperature T. The model system discussed here shows a temperature decrease of up to few degrees Kelvin as the field B is increased at constant entropy.

where $\beta = 1/k_\mathrm{B}T$. The fundamental thermodynamic expression $\mathrm{d}E = T\mathrm{d}S - \mu_z \mathrm{d}B$ yields immediately the Maxwell relation

$$\left(\frac{\partial T}{\partial B}\right)_S = \frac{-(\partial S/\partial B)_T}{(\partial S/\partial T)_B} \quad (3)$$

that describes the temperature response to the external field in isentropic processes. We calculate this quantity using the expectation values of the potential energy U and the z-component of the magnetic moment μ_z of the whole system as

$$\left(\frac{\partial T}{\partial B}\right)_S = -\beta \frac{\langle U\mu_z \rangle - \langle U \rangle \langle \mu_z \rangle}{\frac{6}{2} N k_B + k_B \beta^2 (\langle U^2 \rangle - \langle U \rangle^2)}. \quad (4)$$

3 Results

Our results for S and $\left(\frac{\partial T}{\partial B}\right)_S$ as a function of B_ext and T are represented by contour plots in Figure 1 and Figure 2, respectively [13]. The steps in the isentropes displayed in Figure 1 indicate a temperature decrease with increasing magnetic field at constant entropy. For example, an increase of the field from 45 to 55 Gauss cools the system down from $T = 12$ K to $T \approx 8$ K. The narrow region in the $B_\mathrm{ext} - T$ space, where these kinks occur, separates the chain and ring phases. It is only in this narrow region of the $B_\mathrm{ext} - T$ space that $(\partial T/\partial B)_S$ shows a nonzero value and hence a potential for magnetic cooling, indicated in Figure 2. A closer inspection of Figure 1 shows that the $S =$ const. lines change their slope in the chain phase at high fields, which also corresponds to a positive value of $(\partial T/\partial B)_S$ in Figure 2. This behavior is simply related to the fact that chains behave like a *conventional* magnetic system, since their magnetic and structural order increases with increasing external magnetic field. In the six-particle system discussed above, the conventional cooling mechanism by isentropic demagnetization in high fields is about one order of magnitude less important than the paradoxical magnetic cooling that is related to the ring-chain transition.

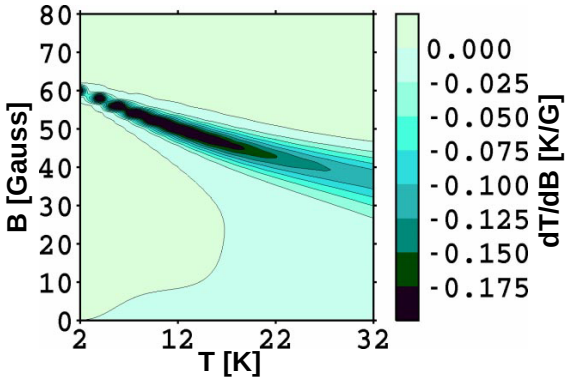

Fig. 2. Contour plot of $(\partial T/\partial B)_S$ as a function the external magnetic field $B_{\rm ext}$ and temperature T.

Let us now discuss some details related to a possible realization of the system. In our simulations we disregarded the internal degrees of freedom of the magnetic particles and the colloidal suspension. Obviously, the cooling efficiency of this particular composite system is highest when the magnetic degrees of freedom of the particles dominate. A potential candidate paradoxical cooling system is a dilute gas consisting of both magnetic particles, which could aggregate, and non-magnetic particles of similar size. The actual thermal transition is initiated by vibrational excitations that lead either to the breakup of rings into chains or a reconnection of chain ends to a ring. Let us now consider a mixture of chains, rings, and other isomers exposed to an oscillating magnetic field. Whereas the breakup energy increases as the neighboring dipoles gradually line up in the larger rings, the vibrational excitation spectrum gets dense especially in the range of low frequencies that drop with $1/N^2$. Hence it is preferentially the larger rings that are broken up to chains by a low-frequency external field. Also the chain structures experience an analogous softening of the vibrational spectrum with the factor of $1/N^2$. Yet due to the larger phase space volume, the likelihood of two chain ends to reconnect to a ring decreases drastically in larger systems.

The chain ends (which are to meet for a chain-to-ring transition) not only move more slowly with larger N but have to explore a much larger space in which the other end can be. The time required for the two ends to reconnect rises dramatically with N, so that chain-to-ring transitions can not be realized in a reasonable time in an ensemble of long chains.

In a realistic experiment, we also have to consider that the average size of the ferrofluid aggregates depends not only on the initial conditions, but increases as a function of time due to further aggregation. To prevent this gradual size increase, we propose to expose the ferrofluid suspension to a low frequency magnetic field that should preferentially break apart the larger aggregates and to stabilize the mixture of prevalent isomers in the region of five to seven particles per aggregate.

Paradoxical magnetic cooling is by no means restricted to the model system discussed here. We believe that the same effect should also occur in other nanostructures, such as transition metal clusters, and even in bulk matter consisting of finite-size substructures. We hope that our results will stimulate a search for experimentally realizable systems that may find application in the fascinating field of ultra-low temperature physics.

References

1. P. Debye, Ann. Physik **81**, 1154 (1926).
2. W.F. Giauque, J. Am. Chem. Soc. **49**, 1864 (1927).
3. R.E. Rosensweig, Sci. Am. **247**, 124 (1984).
4. G.J. Ehnholm *et al.*, Phys. Rev. Lett. **42**, 1702 (1979).
5. Hao Wang, Yun Zhu, C. Boyd, Weili Luo, A. Cebers, R.E. Rosensweig, Phys. Rev. Lett. **72**, 1929 (1994).
6. P. Jund, S.G. Kim, D. Tománek, J. Hetherington, Phys. Rev. Lett. **74**, 3049 (1995).
7. P. Borrmann, H. Stamerjohanns, E.R. Hilf, D. Tománek, S.G. Kim, P. Jund, J. Chem. Phys. **111**, 10689 (1999).
8. D. Tománek, S.G. Kim, P. Jund, P. Borrmann, H. Stamerjohanns, E.R. Hilf, Z. Phys. D **40**, 190 (1997) .
9. Particles of different materials and sizes can be used as constituents of ferrofluids. The present choice of parameters, different from the choice in reference [6], represents a system with a convenient transition temperature.
10. We note that in the present system of magnetic particles, the temperature scales with the magnetic moment of the particles.
11. N. Metropolis, A. Rosenbluth, M.N. Rosenbluth, A.H. Teller, E. Teller, J. Chem. Phys. **21**, 1087 (1953).
12. A.M. Ferrenberg, R.H. Swendsen, Phys. Rev. Lett. **61**, 2635 (1988); A.M. Ferrenberg, R.H. Swendsen, Phys. Rev. Lett. **63**, 1195 (1989).
13. We chose $T = 2$ K as the lower temperature limit for computational reasons that are related to the slow equilibration of a cold system.