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A MONTE CARLO SIMULATION OF CONFINED MAGNETIC SYSTEMS WITH RADIAL BOUNDARY CONDITIONS

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We present a computer simulation of a confined magnetic system. We study a Heisenberg model microsphere with radial boundary conditions, the influence of the homeotropic surface alignment on the magnetic ordering inside the sphere and the consequent changes induced in the thermodynamic behavior. Comparisons with the case of nematic liquid crystal droplets are provided.

1. Introduction

The study of magnetic and nematic ordered systems in a restricted environment has attracted much attention, also for the fundamental interest of the structure of their topological defects.[1–7] The thermodynamic and microscopic behavior of mesophases in confined systems is equally of great interest, as can be seen from the large amount of experimental and theoretical work done on Polymer Dispersed Liquid Crystals (PDLC). These new materials consist of nematic droplets embedded in a polymer matrix and are used in technological applications as electro-optical devices.[8] Similar systems constituted of magnetic grains suspended in an appropriate fluid or polymer matrix form the basis of ferrofluids, see Ref. 9 and references therein. The thermodynamic behavior of superparamagnetic particles in the Néel–Langevin limit where the interaction of different magnetic grains is negligible has been studied by various authors.[10,11] Moreover new technologies for the preparation of microdroplets of sizes as small as $10nm$ are becoming available[12] even though knowledge of the molecular organization inside is still limited. The ordering and the molecular organization inside the system result from the competition and combination of various effects: the boundary conditions, the characteristics of the intermolecular potential, the temperature and possibly the application of an external field.

From a theoretical point of view, PDLC have been studied using Frank elasticity continuum theory of the Landau–DeGennes type[13] and, at microscopic level,

Monte Carlo (MC) simulations of lattice spin models have been performed.[14] In particular we have shown, in a recent series of papers, that MC can be profitably used to investigate PDLC models under a variety of the different conditions above mentioned.[15]

As for magnetic systems, there are until now, to our knowledge, no microscopic MC investigations of the influence of boundary conditions on the spin organization and here we wish to start to tackle this point. The aim of the present paper is thus to study finite spherical lattice spin systems of various sizes, from a few hundred to several thousands of spins, by MC simulation to examine the effect of confinement on the demagnetization phase transition and to calculate order parameters and spatial correlations inside the droplet.

2. The Simulations

We consider a classical cubic Heisenberg model where the spins $\mathbf{S}_i$'s are three-dimensional unit vectors, located at the lattice sites, and interacting through the first rank pair potential[16]:

$$\begin{aligned} U_{ij} &= -\epsilon_{ij}\mathbf{S}_i \cdot \mathbf{S}_j \\ &= -\epsilon_{ij}\cos(\beta_{ij})\,, \end{aligned} \tag{1}$$

where ϵ_{ij} is (for the standard isotropic ferromagnetic case) a positive coupling constant, ϵ, for nearest neighbors spins i and j and zero otherwise. A model magnetic droplet is carved as a jagged sphere from the cubic lattice by considering all the spins falling within a given distance from the chosen center. The radial boundary conditions are mimicked assuming a layer of outside spins (*ghosts*) pointing toward the center of the lattice. This homeotropic surface alignment enforces, especially at low temperature, a point disclination at the center of the system and we have recently applied the MC method to investigate the structure of this hedgehog core defect.[17]

The Heisenberg model is of course well studied in the bulk both by means of approximate theories and computer simulations.[16] It shows a second-order phase transition from the ordered ferromagnetic phase to the disordered paramagnetic phase at a reduced temperature $T^* \equiv kT/\epsilon \approx 1.442929$.[18]

We have used microspheres cut out of cubic lattices of linear dimension $L = 10$ or 24, and containing $N = 304$ and 5832 spins respectively. These two systems are surrounded respectively by 200 and 1352 ghosts. Some other particle sizes (N = 1472, 11752) have been simulated at selected temperatures to look at the scaling with lattice dimension.

The simulations at the various temperatures were run in cascade starting from a perfect hedgehog system or from an equilibrated configuration at the nearest lower temperature. A standard Metropolis algorithm[19] has been employed to update the lattice maintaining a controlled evolution[20] with a rejection ratio not too far from 0.5. At least 30000 equilibrium cycles (i.e. N attempted moves) have been discarded

before accumulating averages and production runs of at least 20000 cycles have been used.

We have calculated several thermodynamic observables: energy, heat capacity, magnetization, order parameters and pair orientational correlation functions. The energy of the system is evaluated as a sum of pair interactions (Eq. (1)). The dimensionless heat capacity C_V^* is obtained by differentiating the average energy with respect to temperature as described in Ref. 21.

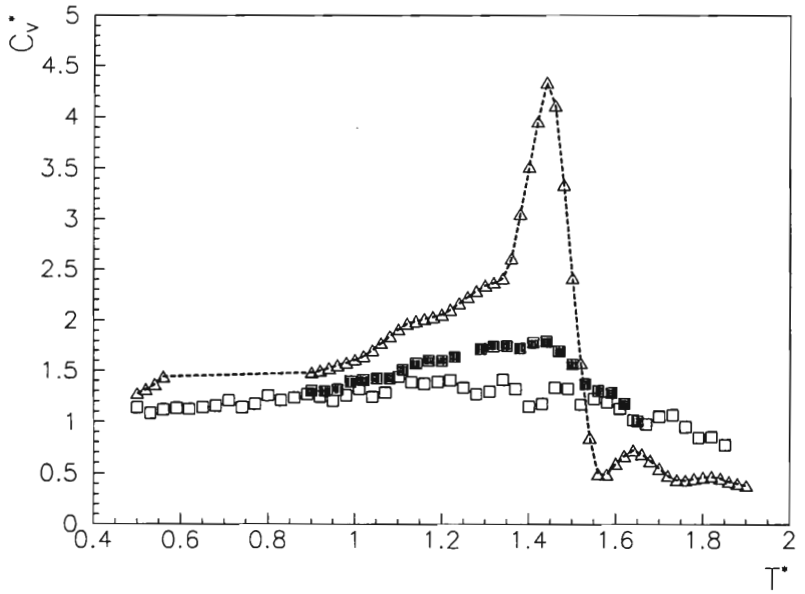


Fig. 1. Heat capacity versus temperature for the two system sizes studied: $N = 304$ (empty squares) and $N = 5832$ (full squares). Results for the bulk[22] from a simulation of a 304 spin droplet (triangles) with cluster boundary conditions are also reported for comparison.

3. Results

We show in Fig. 1 our results for the specific heat for the two grain sizes (*squares*). We first notice that the results of the present model are consistent with a suppression of the phase transition. Similarly to the nematic case, the radial boundary conditions greatly affect the energy and the C_V^* curves appear quite flat. In the results of the larger simulations only a small broadened peak is present, slightly below the bulk critical temperature (see Fig. 1).

These results are certainly a consequence of the surface alignment and are not due to the spherical geometry or to the limited number of spins. This can be seen from a comparison with the curve (*triangles*) for a small droplet containing 304 spins but subject to boundary conditions that mimic the bulk, obtained using Cluster MC as described in Ref. 22. We have shown in turn elsewhere that this system correctly

reproduces the second order phase transition of the Heisenberg model as obtained by various authors.[16,18]

We have determined the magnetization with respect to the instantaneous ordering direction, $\langle M \rangle \equiv \langle P_1 \rangle_\lambda$. This is calculated from the unit vector $\mathbf{S}_i$, and the director $\mathbf{d}^J$ (i.e. the mean direction of the spins of all the system in the Jth configuration) obtained from the eigenvector corresponding to the largest eigenvalue of the ordering matrix. The average over K configurations then gives

$$\langle P_1 \rangle_\lambda = \frac{1}{KN} \sum_J^K \left| \sum_i^N \mathbf{S}_i \cdot \mathbf{d}^J \right| . \tag{2}$$

We see that the magnetization of the whole system, shown in Fig. 2, is $O(N^{-1/2})$ at low temperature, where the effect of the boundary conditions dominates, because the great majority of the spins point toward the center. The $\langle P_1 \rangle_\lambda$ remains at very small values up to high temperatures where the spins are isotropically oriented. However, increasing the temperature we can observe that the $\langle P_1 \rangle_\lambda$ curve tends to grow (approaching the critical region, $T_C \approx 1.44$), and this could be due to the increased freedom of the spins overcoming the effect of the boundary conditions. This behavior is confirmed for both the two system size simulations even though the smaller droplet results cannot be, as expected, lower than $N^{-\frac{1}{2}}$.

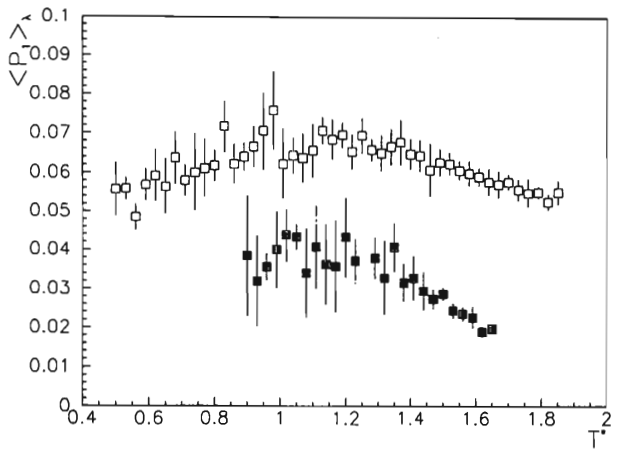
Given that $\langle P_1 \rangle_\lambda$ is rather uninformative, we have calculated, to quantify the deviations from a perfect hedgehog configuration, another quantity that we call first rank *radial order parameter* $\langle P_1 \rangle_R$ defined as follows

$$\langle P_1 \rangle_R = \frac{1}{N} \sum_{i=1}^N (\mathbf{S}_i \cdot \mathbf{r}_i) , \tag{3}$$

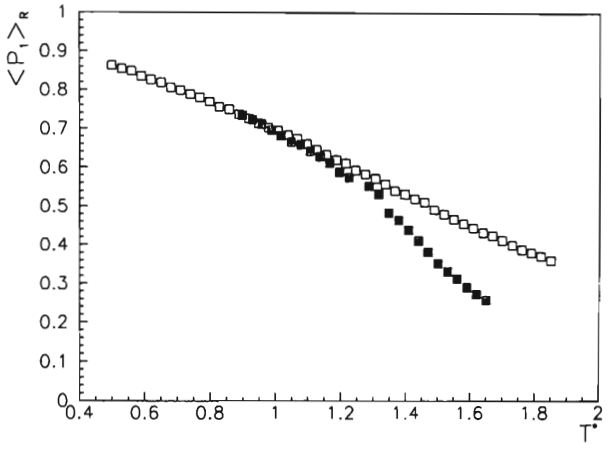
where N is the number of spins contained in the sphere, $\mathbf{S}_i$ is the orientation vector of the ith spin and $\mathbf{r}_i$ is its radial vector. This order parameter expresses disordering from the perfect star-like organization and is a maximum when all the spins point toward the center. The $\langle P_1 \rangle_R$ against temperature curve shows a classical decreasing order parameter behavior (see Fig. 2(b)). The change of the spin organization from a radial configuration to an isotropic one as a function of temperature is now more evident from the simulation results for the larger sample.

We have also investigated how the order parameters change from the center of the droplet to the surface dividing our microsphere into concentric shells in an onion skin fashion.[14b]

The order parameters $\langle P_1 \rangle_\lambda$ and $\langle P_1 \rangle_R$ have been calculated for these different regions and are plotted in Fig. 3 as a function of r. Schopohl and Sluckin[4] have predicted that, for a magnetic system, the radial order parameter should saturate linearly with r according to the existence of a point disclination at the center of the droplet. The simulations support this prediction with results independent from the system size, as shown in Fig. 4 for droplets with 304, 1572, 5832 and 11752 spins.



(a)



(b)

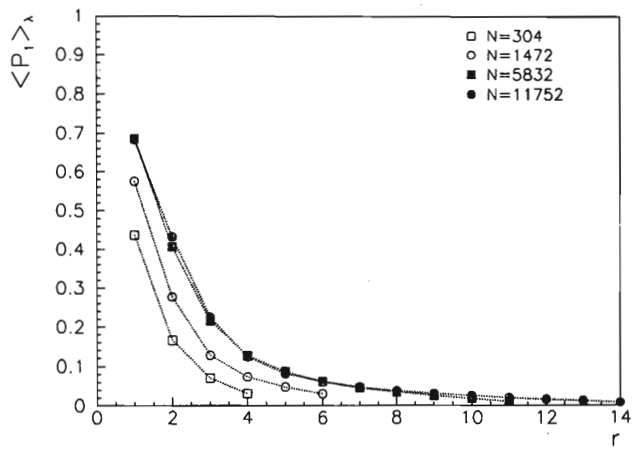
Fig. 2. Magnetization (a) and radial order parameter (b) versus temperature for the two system sizes studied. Symbols are as in Fig. 1.

The present case is thus markedly different from the nematic one for which a larger ordered core consistent with a ring disclination is obtained.[4,17]

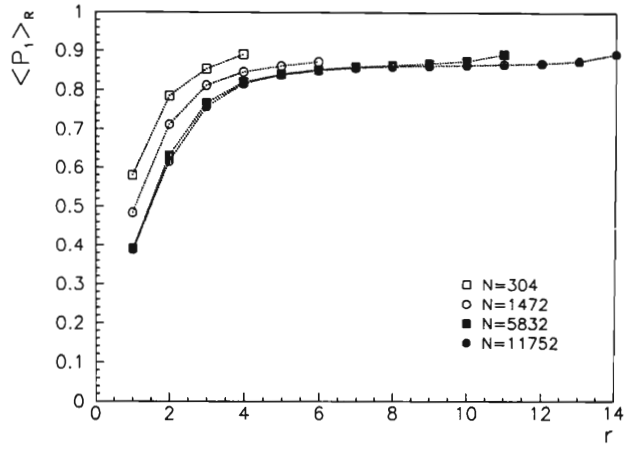
Another indication of the changing of spin organization across the droplet can be glimpsed through the spin–spin correlation function of rank one, defined as

$$G_1(r) = \langle P_1(\cos \beta_{ij}) \rangle_r \tag{4}$$

that gives the correlation between the orientations of two spins separated by a distance r. Here we have investigated the correlation between the spins at a distance



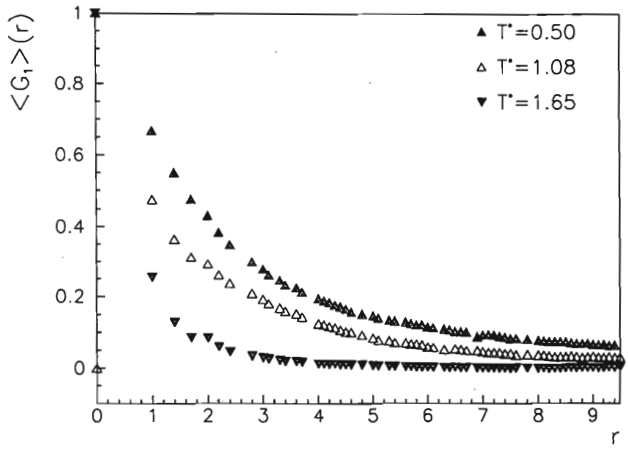
(a)



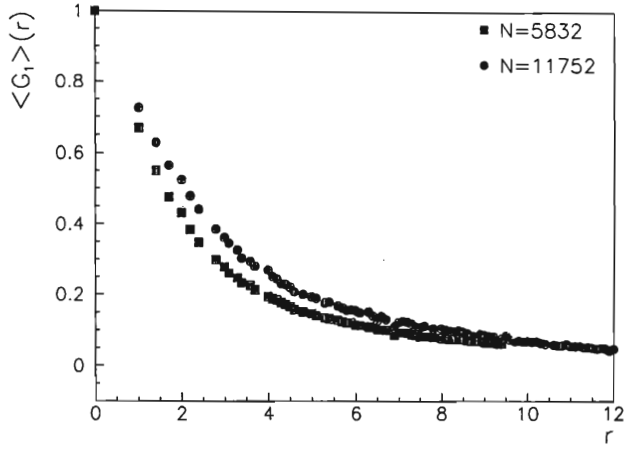
(b)

Fig. 3. Magnetization (a) and radial order parameter (b) from the center toward the surface in lattice units r at $T^* = 0.5$.

r from the center and those as near as possible to the center itself. In practice for the calculation of pair correlations, the eight spins belonging to the $2 \times 2 \times 2$ cube at the droplet center are selected as origins and the pair correlations with all the other particles within a certain range from the central cube are calculated. The overall results for the radial pair correlation coefficients $G_1(r)$ are presented in Fig. 4 for three selected temperatures ($T^* = 0.50, 1.08, 1.65$) and for two system sizes. In a uniform system the pair coefficient $G_1(r)$ starts from one and tails off to essentially the square of the magnetization when the orientation of the two spins becomes not directly correlated. Here the situation is quite different, since spins near the surface



(a)



(b)

Fig. 4. Orientational correlation function versus distance in lattice units r. In (a) results for the microsphere with 5832 spins at three different temperatures are shown. The size dependence at $T^* = 0.5$ is shown in (b).

have an orientation strongly influenced by the boundary layer of spins with pinned orientations. The results confirm that the basic decoupling assumption for spins at the center and at the interface holds for our droplet size. Clearly we expect these results to also hold for large magnetic grains.

In Fig. 5 we show three equatorial sections for the $N = 5832$ droplet, two below and one above the bulk critical temperature. From these snapshots it is possible to have a direct view of the spin organization and to see pictorially the results expressed quantitatively by the order parameters and correlation functions discussed above.

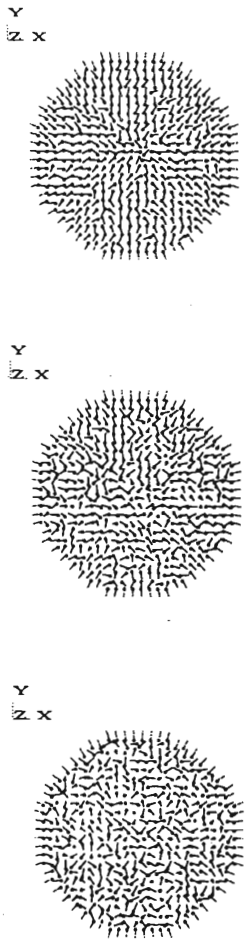


Fig. 5. Equatorial sections of the $N = 5832$ microsphere at three selected $T^* = 0.62$ (top), $T^* = 1.20$ (middle) and $T^* = 1.80$ (bottom).

In fact, at the lowest temperature the point defect near the center of the droplet is clearly identifiable. At increasing the temperature there is a smearing in the influence of the boundary conditions and above the pseudo-critical temperature region the spins are isotropically oriented.

4. Conclusions

We have performed computer simulations of magnetic nano-spheres with radial boundary conditions. The centripetal alignment of the surface spins greatly affects the spin organization inside the system with a depression of the heat capacity peak consistent with an absence of a phase transition. The model could be useful in the investigation of small metallic clusters with a limited number of atoms.[23]

Acknowledgments

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