Vol. 91 (1997) *ACTA PHYSICA POLONICA A* No. 1

Proceedings of the European Conference "Physics of Magnetism 96", Poznań 1996

PROPERTIES OF MAGNETIC NANO-PARTICLES

P.A. LINDGÅRD

Department of Condensed Matter Physics, Risø National Laboratory
4000 Roskilde, Denmark

The intrinsic thermodynamic magnetic properties of clusters are discussed using spin wave theory for a Heisenberg model, with a fixed magnitude of the spins $S_i = S$ and site independent nearest neighbor exchange interaction. The consequences of the more realistic Hubbard model is considered in which we allow for a magnetization profile at $T = 0$ and a structural relaxation, which in turn will give rise to a site dependent exchange interaction. It is concluded that correlation effects among the electrons play a very important role in small clusters, albeit not modifying the thermodynamic properties drastically. The finite cluster size gives foremost rise to a discrete excitation spectrum with a large energy gap to the ground state. The relaxation of the magnetization during the reversal of the external magnetic field is discussed. A first step towards a quantitative understanding of the *nonequilibrium* statistical mechanics in single-domain ferromagnetic particles is a systematic study of the kinetic Ising model. Results from Monte Carlo simulation and droplet theory are reviewed with particular attention to the effects of various boundary conditions, including a decrease in the number of surface bonds and an addition of surface anisotropy. A new dynamic "outside-in" flip mode is proposed.

PACS numbers: 75.30.Ds, 75.40.Gb, 76.20.+q

1. Introduction

In short, small magnetic particles are prime examples of mesoscopic quantum systems. The magnetic properties of clusters of transition metal atoms are in focus in order to elucidate how magnetism evolves from the atom to the bulk. This is of importance for the potential applications of the clusters in recording materials and in catalysts. The intrinsic thermodynamic magnetic properties of clusters are discussed using spin wave theory for a Heisenberg model. The consequences are considered of a quite realistic model, in which we allow for a magnetization profile at $T = 0$ and a structural relaxation, which in turn will give rise to a site dependent exchange interaction. We have also considered longer range interactions and effects of possible enhanced surface anisotropy. The demand for increased storage density in magnetic recording media has prompted a great deal of experimental interest in single-domain ferromagnetic particles, which typically have diameters

of less than one micron, since each can in principle store one bit of data. However, in order to serve as reliable storage devices, the particle must be capable of retaining their magnetizations for long periods of time in arbitrarily oriented ambient magnetic fields i.e. they must have a high coercivity and a large remanence. For both this reason and the more fundamental one: does quantum tunneling occur in mesoscopic systems (a small Schrödinger-cat-problem), the relaxation of the magnetization in small particles is of great interest. A brief review of the present knowledge will be given. As a first step towards a quantitative understanding of the *nonequilibrium* statistical mechanics in single-domain ferromagnets is a systematic study of the kinetic Ising model. Progress in this direction has been made by several authors [1–3]. Richards et al. [4] studied the size dependence of the magnetic switching field for clusters with periodic boundary conditions. Using Monte Carlo simulation and droplet theory we [5] have recently extended this work by considering the effects of free boundary conditions, including the addition of surface magnetic fields or increased number of or strength of the surface bonds, such as may occur as a result of surface reconstruction. The switching field $H_{\mathrm{SW}}(\tau)$ is defined as that magnitude of the reversed field at which the magnetization of the particle on average reverses (passes through zero) for a chosen waiting time τ. This is an important measure for the relaxation. When the clusters become sufficiently large they are no longer "super-paramagnetic" and the dipole energy makes them split up into domains which can close the field lines. The classical theory [6] therefore predicts $H_{\mathrm{SW}}(\tau) = 0$ for sufficiently large clusters (particles). However, Richards et al. [4] found that there is an optimum $H_{\mathrm{SW}}(\tau)$ even when neglecting the dipole effect. Thus, there seems to be a much smaller optimum cluster size for memory properties at least for clusters with periodic boundary conditions or sufficiently long waiting times. This feature is also found for the new dynamic flip model, here proposed.

First, we address the intrinsic thermodynamic magnetic properties using the spin wave theory [7, 8] for an effective Heisenberg model. The spin wave theory at finite temperature and the thermodynamics for the itinerant magnets are exceedingly difficult [9]. However, it is a good approximation to consider that the $3d$-electron spins around a site i are performing a coherent precession which can be represented by the precession of an effective Heisenberg spin S_i. Detailed investigations by in particular Pastor, Dorantes-Dávila and collaborators [10] using the Hubbard model, have shown that for small clusters the magnetic moment increases strongly towards the surface of the cluster, the cluster structure is relaxed — and in addition the average moment in the clusters is larger than in the bulk. The results by Pastor et al. [10] will form the basis for the present discussion of the influence of the electronic modifications on the thermodynamic magnetic properties of nanometer sized particles. A recent similar study of the $4d$ metal clusters [11] also shows strong effects of the electron correlations, in particular by making some materials, like Rh, magnetic in the nano-particle size.

Experimental investigations of unsupported Fe- and Co-clusters have indeed indicated that the atomic magnetic moments are larger in the clusters than in the bulk [12]. Neutron scattering experiments of 2–3 nm iron particles in an aluminia matrix have recently been reported [13]. Further scattering measurements

on clusters in less active media, e.g. the noble gases, would be of great interest, in particular also inelastic measurements. The reduction of the number of nearest neighbors for the atoms at the surface is expected to decrease the effective transition temperature T_c to magnetic order inside the clusters, as also found in our actual calculations [7,8]. However, experimentally it has been reported [14] that T_c is not reduced relative to that for the bulk. This represents a puzzle.

Any change in the surface restoring force preventing the creation of a spin flip (or deviation) will have a drastic effect on the relaxational behavior. Thus a reduction in the coordination number would favor spin reversal of the cluster to start from the surface. Contrary, an increased surface anisotropy or larger surface moments or interactions will counterbalance that effect. We shall in the following assume that the spin structure of the small cluster is collinear. It is known that both surface anisotropy [8] and long-range interactions [15] can cause the structure to be canted. However, for the spin wave theory, which follows, this only represents a small technical problem of going over to a local coordinate system with proper quantization axis. This modifies the interaction without changing the basic physics.

2. Theory

The theory of the magnetic excitations and the method of calculation have recently been described in detail [7,8], therefore only a few basic steps will be given here. We consider an effective (collinear) Heisenberg model

$$\mathcal{H} = -\frac{1}{2}\sum_{ij} J_{ij}\boldsymbol{S}_i \cdot \boldsymbol{S}_j. \tag{1}$$

We shall allow both the exchange interaction J_{ij} and the spin values S_i at $T = 0$ to vary with the sites i, j in the cluster. We have also considered the effect of interactions beyond the nearest neighbors. This is usually required in order to describe the spin waves for the transition metals by an effective Heisenberg model. The equation of motion for the spin deviation operator S_i^+ for a ferromagnetic cluster can in a symmetrized, site-dependent random phase approximation be written [8]

$$\hbar\omega S_i^+ = \sum_j A_{ij} S_j^+,$$

where

$$A_{ii} = \sum_j J_{ij} M_j, \qquad A_{ij} = -J_{ij}\frac{M_i + M_j}{2}. \tag{2}$$

$M_i = \langle S_i^z \rangle$ is the thermally averaged mean value of the spin at site i, which is to be calculated self-consistently. By iteratively improving the M_i-profile the eigenvalue problem can be solved by a direct numerical diagonalization, yielding both the N discrete eigenvalues E_p and the corresponding (normalized) eigenfunctions ψ_i^p describing the value of S_i^+ for each state p. In a classical picture the amplitude S_i^+ can be considered to be the opening radius of the cone on which the spin at site i precesses, $S^+(t) = S^+ \exp(i\omega t)$. In the bulk case the amplitude $S_j^+ = S^+$ is site independent, and the different states are characterized by a wave vector $\boldsymbol{q}$ and a site dependent phase factor $\exp(i\boldsymbol{q} \cdot \boldsymbol{r}_j)$ for the site at $\boldsymbol{r}_j$ (Bloch-states). In the clusters the eigenstates have site dependent amplitudes, and surprisingly

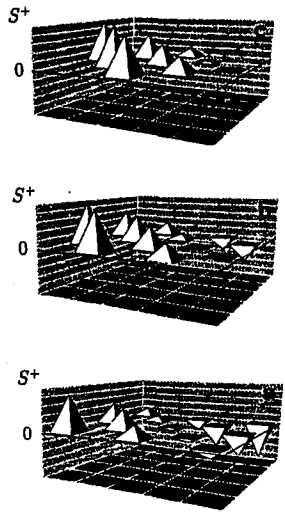

Fig. 1. The wave function of the first excited state of a bcc 55-spin-cluster illustrated in real space for the upper half of the cluster (one of three triply degenerate states). The cluster has been cut along the [100] planes: (a) is the central plane and (b) and (c) the two upper planes. The height of the spikes indicates the magnitude of S^+, and the direction (up or down) indicates the sign. A change in sign corresponds to a phase shift in the precession movement of 180°. The behavior of the lower half of the cluster is given by inversion around the center.

we find for the investigated cluster sizes that the spins are precessing in exact phase or anti-phase on the opposite sides of the cluster, see Fig. 1, which shows the wave function ψ_i^p for one of the first excited states, p. It is intriguing to imagine how these states evolve into Bloch states for infinite cluster sizes. The variable amplitude is a consequence of the open boundary conditions. For clusters embedded in a magnetic medium these would change and one would expect less variation with site. The states with the minimum relative change from site to site and few nodal planes have the lowest energy, i.e. those with large amplitudes at the surface. Since these states are first populated at finite temperatures it is clear that a more rapid decrease in the magnetization is predicted for the surface layers. The magnetization is given by [8]

$$M_i(T) = S - \sum_{p=1}^{N-1} |\psi_i^p|^2 n_p, \tag{3}$$

where $n_p = [\exp(E_p/k_B T) - 1]^{-1}$ is the Bose weight of the state p, and $|\psi_i^p|^2$ is the quantum-mechanical probability of finding the spin deviation at i. The neutron scattering cross-section $S(q,\omega)$ is also given in terms of the eigenfunctions

$$S(q,\omega) \propto \sum_{p=1}^{N-1} |\sum_j \psi_j^p e^{iq\cdot r_j}|^2 \delta(\hbar\omega - E_p). \tag{4}$$

Finally, the effective transition temperature T_c (determined by a maximum susceptibility criterion) can be calculated using a generalization of the spherical approximation [8]. It is the temperature $T = T_c$ which fulfills the following equation for $1/\chi \to 0$:

$$\frac{T_c^{MF}(\text{bulk})}{T} = \frac{1}{N-1}\sum_{p=1}^{N-1}\frac{1}{1/\chi + E_p/J_0 S}. \tag{5}$$

Here $T_c^{MF}(\text{bulk}) = J_0 S(S+1)/3k_B$, $J_0 = \sum_\rho J_{i=0,i+\rho}$, where ρ is a nearest neighbor index, and χ is the cluster analog of the uniform susceptibility. Equation (5) allows also $\chi(T)$ to be evaluated as a function of temperature for $T > T_c$.

3. Results

First, let us summarize some of the results obtained assuming, at $T = 0$, where $S_i = S$ is site independent and considering only nearest neighbor (nn) interaction $J_{ij} = J_1\delta(i-j+\rho)$. The neutron scattering cross-section is shown in Fig. 2 for two high symmetry directions of q, (a) [100] and (b) [110] for a 59 bcc cluster. It shows a discrete spectrum and a large energy gap ΔE to the first excited state. The order of magnitude of ΔE is $\Delta E/k_B \approx 30$ K for a 749 spin α-iron cluster and ≈ 140 K for a 9 spin cluster. The spectrum is broadened in the wave vector q, since q is not a good quantum number, as it is in the bulk case. We notice that although the states p are the same, only a few can be seen simultaneously for q in the different directions. Notice in particular that the lowest state is visible in both directions. In a sample containing randomly oriented (mono-disperse) clusters we expect $S(q,\omega)$ to show all the p energy levels, only slightly more broadened in q than in the high symmetry directions, Fig. 2. We remark that most of the levels are at least 3 times degenerate in energy due to the cubic symmetry. This should make the gaps easier to detect experimentally. Random perturbations of the structure, and thereby random modifications of J_{ij}, lift the high degeneracy of the spectrum [8] smearing the energy gaps, but it has little influence on the thermodynamics of the system. The spectrum (E_p) is of course different for clusters with different number of spins. Therefore, for a poly-disperse sample of clusters there is an additional smearing of the energy gaps, but ΔE should still be clearly observable. The presence of the large energy gap is a direct consequence of the

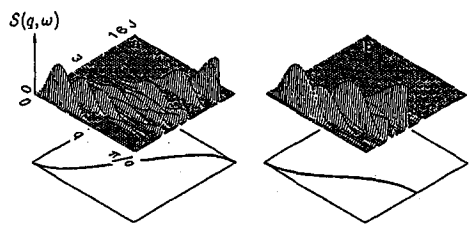

Fig. 2. Neutron scattering cross-section $S(q,\omega)$ calculated for q in the (a) [100] and (b) [110]-direction for a bcc cluster containing 59 spins. The solid curves in the lower plane are the bulk dispersion curves in the same directions.

smallness of the clusters. This energy gap is much larger than the contribution to the gap coming from single site crystal field anisotropy or from the largest available external magnetic fields [8]. This is important, because it shows that the excitations in some sense resemble those of strongly anisotropic model, like the Ising model, rather than the Heisenberg model. This partly motivates why it makes good sense to perform the relaxation studies using the simpler Ising model.

The energy gap ΔE gives in principle rise to an exponential behavior of the mean magnetization deviation $\Delta M(T) = S - \frac{1}{N}\sum_i \langle S_i^z \rangle$. However, a good fit can be made to an effective power law

$$\Delta M(T) = BT^{\alpha}, \tag{6}$$

in a large temperature interval, up to 35% of T_c. The effective exponent α decreases linearly from about 3 to the bulk value 3/2 as a function of decreasing inverse cluster radius $1/r_c$. The constant B depends (as in the bulk case) on the average number of neighbors per site and is thus dependent on the structure of the cluster. The exponent is *independent* of the structure (bcc, fcc or random) for a cluster containing the same number of spins. A power-law temperature dependence of the magnetization with a larger than bulk exponent has indeed been found experimentally for 3 nm Fe/C-particles by Linderoth et al. [16] in good agreement with the theory [7,8]. In Fig. 3 the magnetization is shown as a function of T and reciprocal cluster radius $1/r_c$ for the center spin (short-dashed line), the average moment (full line) and the outer shell (long-dashed line). The average moment calculated by the spin wave theory extrapolates naturally (thin line) to the T_c as calculated from Eq. (5). For a 51 bcc cluster T_c is found to be reduced to 59% of the bulk value T_c(bulk). For increasing cluster sizes, T_c is seen (thin dashed line) to approach T_c(bulk) for $1/r_c \to 0$, following an expected scaling behavior [8]. Summarizing, we have found that the magnetic behavior of the clusters is significantly different from that of the bulk, with a larger effective magnetization exponent $3/2 < \alpha < 3$ which is independent of the structure and perturbations of the structure. Further, a rapidly decreasing surface magnetization and a substantially reduced T_c, scaling with the average coordination number per spin are found. It is clearly of interest to investigate how robust these conclusions are to

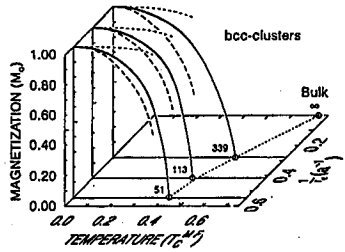

Fig. 3. The calculated magnetization versus temperature and inverse cluster radius $1/r_c$ of the center spin (short-dashed), the average magnetization (full line) and that of the outer shell (long-dashed). The thin lines extrapolate to the calculated T_c from Eq. (5). The number of spins are indicated as well as T_c(bulk) for $1/r_c = 0$.

the electronic modifications of the model. These modifications are expected to be relevant for small metallic clusters.

4. Influence of electronic properties, structural relaxation

Only for the smallest clusters with a few atoms the electronic and structural properties are calculated from first principles. Since we are here interested in nanometer sized particles we shall base our discussion on the calculation of the moment distribution in a $N = 51$ unrelaxed bcc iron cluster by Pastor et al. [10]. They used the unrestricted Hartree–Fock decoupling of the Hubbard model, which can be written schematically (neglecting the band indices)

$$\mathcal{H}_{\rm el} = \sum_{i \neq j,\sigma} t_{ij} c^{\dagger}_{i\sigma} c_{j\sigma} + \sum_{i,\sigma} \epsilon_{i\sigma} c^{\dagger}_{i\sigma} c_{i\sigma} - E_{dc},$$
$$\epsilon_{i\sigma} = \epsilon^0_d + U\Delta n(i) - \frac{1}{2}\sigma \mathcal{J}\mu(i), \tag{7}$$

where t_{ij} is the tight binding hopping term, σ — the spin index, and $U\Delta n(i)$ is a "penalty field" term. This strongly discourages large (square) amplitudes of $|c^{\dagger}_{i\sigma}|^2 = \hat{n}_\sigma(i)$ in the outer shells in order to minimize charge transfer $\Delta n(i) = n_\uparrow(i) + n_\downarrow(i) - n_0$ in the presence of the large Hubbard U term, $n_\sigma(i) = \langle \hat{n}_\sigma(i) \rangle$ is the number of electrons (charge) around site i and n_0 is the average charge. The magnetic moment in units of $\mu_{\rm B}$ is $\mu(i) = n_\uparrow(i) - n_\downarrow(i) \propto S_i$ of Eq. (1,2), and the exchange integral $\mathcal{J}$ splits the $\sigma = \uparrow$ and $\downarrow$ states. E_{dc} and ϵ^0_d are constants. The diagonalization problem of Eq. (7) for $c^{\dagger}_{i\sigma}$ is identical with that for S^+_i in Eq. (2). For the statistics one must remember that electrons are fermions, whereas the spin deviations behave as bosons. It is instructive, as an alternative to the traditional projected density of states argument [10], to think about the problem in terms of the wave functions found for the spin wave problem. For illustration we have calculated the tight binding result, i.e. not including the $U\Delta n(i)$ term in Eq. (7). By filling up the electrons to the Fermi energy in the spin split states the large amplitude surface states for both $\uparrow$ and $\downarrow$ get rapidly filled up and cancel in $\mu(i)$; consequently the tight binding approximation suggests a decreasing moment towards the surface. For the electrons it is essential to include the charge transfer penalty, which strongly mixes the states in energy since U/t_{ij} is large. The shell moment for a 51 unrelaxed bcc-iron cluster calculated self-consistently [10] including the penalty term Eq. (7) increases above the bulk value at the surface. A lower than average moment in the center and a strongly increasing moment S_i for the outer shells were found. This can easily be incorporated in the solution of Eq. (1). Calculating $M_i(T)$ self-consistently from Eq. (3) and fitting to Eq. (6) we find *no change*, within the uncertainty of the fit, relative to the uniform case. Using Eq. (5) we find a small increase in $T_{\rm c}$ of 5%, mainly due to the larger average moment $\mu_0 = 1.10\mu$(bulk) found for the cluster by Pastor et al. [10]. The calculated magnetization extrapolates naturally to the calculated $T_{\rm c}$.

Another modification to consider is variations in J_{ij} due to structural relaxation of the cluster, which can strongly alter the overlap terms in the exchange integrals. In an unrelaxed cluster it is not possible to have a non-uniform moment distribution at $T = 0$ without a certain charge transfer. Suppose for simplicity

that we have fully occupied ↑ bands $n_\uparrow(i) = n_\uparrow^0$ therefore the moment variation arises solely from the ↓ bands $n_\downarrow(i) = n_\downarrow^0 + \Delta n(i)$. Then it is easy to see that the charge transfer is related to the moment profile by $\Delta n(i) = \mu(\text{bulk}) - \mu(i)$. Let us make a crude model for the lattice relaxation by requiring that the electron density around each nucleus is equal to that of the bulk and enforcing this by adjusting the Wigner–Seitz radius r_{WS} to account for excess electrons. For iron (atomic state: argon-$3d^6 4s^2$) with 8 conduction electrons per nucleus we then argue as follows. In a sphere with volume $\frac{4\pi}{3} r_{\text{WS}}^3$ there are 8 electrons in the bulk, whereas for the cluster there are $8 + \Delta n(i)$ in the volume $\frac{4\pi}{3} r_i^3$. Consequently, we need to adjust the radius as $r_i = r_{\text{WS}}[1 + \frac{1}{3\times 8}\Delta n(i)]$. We now distort the bcc cluster by packing these spheres of unequal radii ($0.98 r_i$). The relative distance between the spins can be written $r_{ij} = R + \Delta r_{ij} = R\{1 + \frac{1}{48}[\Delta n(i) + \Delta n(j)]\}$, where $R = a\sqrt{3}/2$ is the bulk distance. We apply the argument to the 51 bcc cluster studied by Pastor et al. [10]. The result is an expansion of the core of the cluster and a contraction of the outer shells, with lattice constant changes of the order of 1%, as generally expected [10]. For all atoms the displacements are along the cubic symmetry directions, except for the outermost shell, which is more drastically reconstructed. However, the nearest neighbor coordination number is *unchanged* by these displacements and the bond directions are only slightly modified. Now, suppose the exchange constant in Eq. (1) depends strongly on the distance between the spins $J(R + \Delta r) \approx J(R)(1 + x\frac{\Delta r}{R})$, where $|x| \approx 10$. The site dependent Heisenberg interaction in the relaxed cluster is then

$$J_{ij} = J(r_{ij}) \approx J(R)\left\{1 + \frac{x}{48}[\Delta n(i) + \Delta n(j)]\right\}. \tag{8}$$

This modification of J_{ij} can effectively be included in Eq. (1), by using $J_{ij} = J(R) = J_1$ and instead introducing the effective moments $\mu_{\text{eff}}(i) = \mu(\text{bulk}) - (1 - \frac{x}{48})\Delta n(i)$. Notice that for $x = 0$ we have the unrelaxed result [10]. For iron x is expected from various experimental facts [17] to be positive $x \approx +10$. Therefore, including the lattice relaxation in this crude model tends to effectively reduce the moment profile and only perturb the already minimal effect of a magnetization profile for iron.

A more effective way of influencing T_c might be if the lattice distortions were able to change the average coordination number. Even when making the unrealistic assumption that all surface atoms have reconstructed to a closed packed coordination, all else equal, T_c is only raised by a few %. However, for the relaxation properties, the nature of the surface is playing a dramatic role in defining the minimum energy barrier needed to overcome in the flip process and in determining where the process may initiate.

5. Magnetic relaxational behavior

Small magnetic particles exhibit so-called superparamagnetism [18], which means that they at a certain level of description, namely the thermodynamical, behave as a giant spin $\mathcal{S} = \sum \mathcal{S}_i$ consisting of the sum of all the individual ones. It would be highly interesting if the picture holds also in a quantum-mechanical sense, such that the particles have only two states relative to an external field parallel or anti-parallel: $|\mathcal{S}^z\rangle = |\pm\rangle$. If the states are separated by a (fixed) barrier we

would have a nice physical representation of the fundamental double well problem in quantum mechanics. The theory for this and the relation to micro-magnetism has been long discussed by Leggett et al. [19]. The essential result is that there is a quantum-mechanical escape-rate Γ from a metastable state which does not exist in classical physics. The logarithm of Γ is proportional to the barrier height V_0 (and width), divided by the attempt frequency ω_0, but not temperature. A similar thermodynamical (classical) rule was formulated by Arrhenius [20] in which enters the barrier height divided by the temperature. Thus we have two possibilities for the decay in magnetization M (an indicator of the occupation of the metastable state). From a damped harmonic oscillator equation or a Langevin-type equation $\frac{\mathrm{d}}{\mathrm{d}t}M \propto -\frac{\delta}{\delta M}F + \text{r.f.}$ where the free energy F (thermodynamic potential) is assumed to be of the form $F = \frac{1}{2}M^2/\chi + \frac{1}{4}bM^4 + \ldots$, we then expect the relaxation to be exponential for the double well potential

$$\frac{\mathrm{d}}{\mathrm{d}t}M(t) = -\Gamma M, \qquad M(t) = M_0 \exp(-\Gamma t), \tag{9}$$

where the kinetic coefficients in the quantum-mechanical (QM) and thermodynamic (TH) cases, respectively, are

$$\Gamma \propto \exp(-V_0/\hbar\omega_0) \quad \text{(QM)}, \quad \Gamma(T) \propto \exp(-V_0/k_\mathrm{B}T) \quad \text{(TH)}. \tag{10}$$

There are indeed experimental systems in which the relaxation is not found to decrease even when cooling to very low temperatures [21]. However, since long it has been known that the magnetic relaxation is usually not following the exponential decay (9) as e.g. found in the decay of unstable nuclei. A variety of other time dependences for $M(t)$ has been proposed, including stretched exponential behavior. A commonly accepted dependence is a logarithmic decay after a chosen time t_0

$$m(t) = \frac{M(t)}{M(t_0)} = [1 - A(T)\ln(t/t_0)]. \tag{11}$$

This can be derived both in the case where one assumes a distribution of barrier heights, and in the case where one assumes a single barrier height, which depends on $M(t)$, linearly. This can easily be seen from (9) [21]. The often observed dependence (11) has lead to the introduction of an experimental concept, the magnetic viscosity (conventionally denoted S), defined as

$$S(T) \equiv \left|\frac{\mathrm{d}m(t)}{\mathrm{d}\ln t/t_0}\right| \equiv A. \tag{12}$$

The kinetic coefficient A defined in this way is supposed to be related to Γ in (10) as $A \propto 1/\ln\Gamma$. Thus $S(T)$ is supposed to be proportional to T in the classical case, but to level off at low T if the quantum tunneling takes place. This is indeed seen for e.g. Dy clusters on a Cu matrix [21]. Experimentally the situation is made difficult because it is hard to obtain mono-disperse systems, i.e. ensembles of identical, non-interacting particles, supposed to have just one type of energy barrier.

Most likely the simple double well representation of the problem is much too simplified for a reliable description at the level of the relaxation phenomena. In a first attempt to attack the problem from a modern statistical mechanics point of view Richards et al. [4] studied the relaxational behavior as a function of size

of small Ising systems. We have in the first part of the paper demonstrated that the energy spectrum is discrete with gaps of the order of magnitude of a significant fraction of the Heisenberg interaction energy, roughly: $\Delta E = cJS/N^{\frac{2}{3}}$, where $c^3 = 4\pi^4/3$. Therefore, the Ising representation is probably even a superior simplified model to use for the Monte Carlo simulations, than a straightforward, classical simulation of the Heisenberg model [3] which neglects the quantum-mechanical discreteness due to the size effect. For simplicity periodic boundary conditions were chosen by Richards et al. This was to eliminate that the spin flip would start (nucleate) at any particular place in the "cluster" and the problem became similar to a usual first-order transition from a metastable state to a stable one. For this it is well known that there exists a *spinodal line* in the (T, H) plane, which (roughly) separates the growth mechanisms into (i) growth by nucleation of a supercritical droplet (ii) exponential growth of magnetization waves. It was found that the magnetization reversal of the clusters was of the nucleation type with several new regimes. (a) For very small clusters the thermal excitations were sufficient to spontaneously flip the magnetization even in zero field, therefore $H_{\rm SW}(T) = 0$, (b) a maximal switching field $H_{\rm SW}(T)$ was found near the thermodynamic spinodal line, (c) a decrease was found at a "dynamic spinodal line" at which the coalescence of several droplets nucleated at different positions dominated the flip process. A thermodynamic theory for the formation of the droplets, taking into account the unfavorable interface free energy and the favorable interior free energy gave a quantitative description of the behavior. In Fig. 4 there is shown the size dependence obtained by Monte Carlo simulation, demonstrating a clear maximum of $H_{\rm SW}(T)$ even without dipole forces included, just for the reason of different flip mechanisms.

However, this study neglects one of the most important features of small particles, namely the presence and the dominant influence of the surface. To investigate the effect of that, various surface configurations without any singular points were investigated, such as semiperiodic systems and free, circular or octangular systems with the number of neighbor bonds, which could be varied from equal to that in the bulk to half of that in the bulk, see Fig. 5. Further, the effect of increasing the surface bond strength, and of adding an anisotropy surface field were studied. The main effect of the presence of a surface at which it costs less energy to flip a spin, is that the nucleation is initiated at the surface and a critical droplet size is reached before the previously studied bulk nucleated droplets can play a role. The switching field is therefore much reduced, as can be seen in Fig. 4. In particular, for short waiting times the peak in $H_{\rm SW}(T)$ as a function of system size disappears in the simulated results. For very large systems the bulk regains the dominant role and subsequently the nucleation in the bulk becomes the most likely for entropy reasons. Then, $H_{\rm SW}(T)$ is predicted to decrease again for sufficiently large systems even in the open boundary cases and without invoking the dipole effect, which is in fact found by the Monte Carlo simulation for long waiting times.

Characteristic of the magnetic switching process is that after a critical size droplet is formed, the switch happens very rapidly, seen on the scale of the average waiting time. Therefore it is not a wild assumption to assume that it happens in

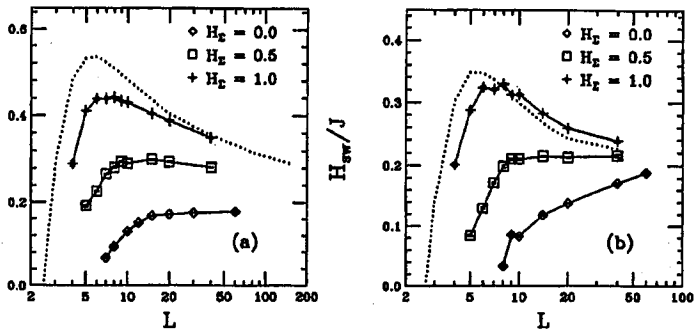

Fig. 4. The switching field as a function of system size obtained by MC for periodic systems (dashed lines, [4]) and octagonal systems [5] with half the number of the bulk bonds at the surface, for various values of the surface field H_Σ (in units of the Ising interaction J). (a) $T = 1.3J \approx 0.5729T_c$ and $\tau = 1000$ MCSS, (b) $T = 0.8T_c$ and $\tau = 100$ MCSS.

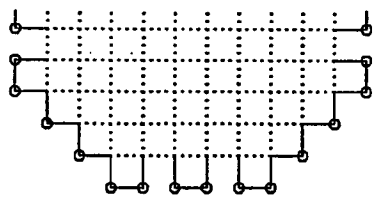

Fig. 5. Example of a constructed surface with a definite number of neighbor bonds: part of a specially constructed octagon where all surface sites have two bonds (half that in the bulk). Similarly a spherical cluster with reconstructed surface has been constructed such that all spins have 4 bonds, including those at the surface.

as "instantaneous" jump between two states. The transition state, which in the sense of quantum mechanics is a superposition state, is in the classical Monte Carlo simulations simply an intermediate growing state. Each spin flip is governed by the Metropolis rule: gain energy if possible, and loose an energy V by the "probability" $\exp(-V/k_BT)$. The growth stops at $T \to 0$. Therefore, such simulations [5,3] cannot strictly speaking shed light on the quantum tunneling problem, although they are very useful in understanding the general non-equilibrium behavior at higher temperatures. Probably, the quantum-mechanical flip process (in which each spin is allowed to tunnel to another state) is somewhat similar to that here found at higher temperatures, indicating that the picture with a single total barrier is far too simplified — whereas a M-dependent barrier seems more reasonable. This would support the experimental finding of non-exponential relaxation (9) and rather a logarithmic dependence (11).

We may get a rather different picture of the switching event if we go back to the spin wave calculation for the more realistic Heisenberg model. Although not exact, this method retains a number of important quantum effects, special for the small cluster problem. We found that the (triply degenerate) first excited states

gave the largest amplitude for spin deviations close to the surface. In these states the spins at opposite sites in the cluster are precessing in exact antiphase and represent a dynamical tilting of the spins in the direction of a reversed external field. The field reduces the energy gap and makes the mode go soft, indicating that the chosen parallel ground state ceases to be valid. In the random phase approximation we can populate the state by many independent (opposite) spin deviations, the more the smaller the energy gap, which is reduced with the decreasing surface magnetization. Going beyond the linear spin-wave approximation, additional phase related excitations with large amplitudes at the surface will be created, and so on, lowering the energy further as a non-linear function of the field. A soft mode scenario then arises in which the flip process can be described by a concerted flipping of the surface spins (opposite surface spins canting in opposite directions). If a sufficiently large amplitude wave is created, the central spins are carried along, much like inverting a sock. We shall call this an "outside-in" flipping. This flip mode differs obviously from the nucleational picture offered by the Ising Monte Carlo simulations, where a concerted wave-like option is not considered. It also differs from the classical Brown–Néel assumption of a uniform rotation or of a single domain wall propagating through the cluster, a picture inspired from bulk behavior. Since the energy gap decreases with particle size the switching field also decreases. At very small sizes we, as above, expect spontaneous flipping and $H_{SW} = 0$. Thus we argue that there is also an optimum H_{SW} for the "outside-in" flip model, without invoking dipole effects.

6. Conclusion

We have considered extensions of the nearest neighbor Heisenberg model and shown that our results are robust to the most compelling intrinsic modifications. In particular, we have found that the effective magnetization exponent is invariable. The inclusion of a magnetization profile and of lattice deformations at $T = 0$ for the $N = 51$ cluster does not alter the calculated T_c significantly; it is reduced to about 60% of the bulk value T_c(bulk). Similar conclusions will hold for larger N. We have considered models for the magnetic relaxation of the small particles. Simulations for an Ising model show the possibility of having an optimum size with respect to achieving a large switching field. This depends sensitively on the assumed boundary conditions. A new scenario for the flipping in terms of the states obtained in the spin wave theory is outlined.

Acknowledgments

It is a pleasure to thank my colleagues who have participated in this work, in particular P.V. Hendriksen, S. Linderoth, S. Mørup, and H.L. Richards.

References

[1] K. Binder, H. Rauch, V. Wildpaner, *J. Phys. Chem. Solids* **31**, 391 (1970); K. Binder, *Physica* **62**, 508 (1972).

[2] J. Merikoski, J. Timonen, J. Mannien, P. Jena, *Phys. Rev. Lett.* **66**, 938 (1991).

[3] P.A. Serena, N. Garcia, in: *Quantum Tunneling of Magnetism — QTM'94*, Eds. L. Gunther, B. Barbara, Kluwer Acad. Publ., The Netherlands 1995, p. 107.

[4] H.L. Richards, S.W. Siders, M.A. Novotny, P.A. Rikvold, *J. Magn. Magn. Mater.* **150**, 37 (1995); *J. Appl. Phys.* **79**, 5749 (1996).

[5] H.L. Richards, M. Kolesik, P.-A. Lindgård, P.A. Rikvold, M.A. Novotny, to be published.

[6] L. Néel, *Ann. Géophys.* **5**, 99 (1949); W.F. Brown, *Micromagnetics*, Wiley, New York 1963.

[7] P.V. Hendriksen, S. Linderoth, P.-A. Lindgård, *J. Phys. C* **31**, 5675 (1993).

[8] P.V. Hendriksen, S. Linderoth, P.-A. Lindgård, *Phys. Rev. B* **48**, 7259 (1993).

[9] T. Moriya, *Magnetic Fluctuations in Itinerant Electron Magnetism, Springer Series in Solid State Physics 56*, Springer, Berlin 1985.

[10] G.M. Pastor, J. Dorantes-Dávila, K.A. Bennemann, *Phys. Rev. B* **40**, 7642 (1989); J. Dorantes-Dávila, H. Dreyssé, G.M. Pastor, *Phys. Rev. B* **46**, 10432 (1992); A. Vega, J. Dorantes-Dávila, L.C. Balbás, G.M. Pastor, *Phys. Rev. B* **47**, 4742 (1993).

[11] B. Piveteau, M.-C. Desjonquères, A.M. Oleś, D. Spaniard, *Phys. Rev. B* **53**, 9251 (1996).

[12] J.P. Bucher, D.C. Douglass, L.A. Bloomfield, *Phys. Rev. Lett.* **66**, 3052 (1991); S.N. Khanna, S. Linderoth, *Phys. Rev. Lett.* **67**, 742 (1991); S. Linderoth, S.N. Khanna, *J. Magn. Magn. Mater.* **104-107**, 1574 (1992); D.M. Cox, D.J. Trevor, R.L. Whetten, E.A. Rohlfing, A. Kaldor, *Phys. Rev. B* **32**, 7290 (1985).

[13] I. Mirebeau, C. Bellouard, M. Hennion, J.L. Dormann, C. Djega-Mariadassou, M. Tessier, *J. Magn. Magn. Mater.* **104-107**, 1560 (1992); J.R. Childress, C.L. Chien, J.J. Rhyne, R.W. Erwin, *ibid.*, 1585 (1992).

[14] Z.T. Tang, C.M. Sorensen, K.J. Klabunde, G.C. Hadjipanayis, *Phys. Rev. Lett.* **67**, 3603 (1991); P.J. van der Zaag, A. Noordermeer, M.T. Johnson, P.F. Bongers, *Phys. Rev. Lett.* **68**, 3112 (1992); V.A.M. Brabers, *Phys. Rev. Lett.* **68**, 3313 (1992); D.C. Douglas, J.P. Bucher, Bloomfield, *Phys. Rev. Lett.* **68**, 1774 (1992).

[15] D.P. Pappas, A.P. Popov, A.N. Anisimov, B.V. Reddy, S.N. Khanna, *Phys. Rev. Lett.* **76**, 4332 (1996).

[16] S. Linderoth, L. Balcells, A. Labarta, J. Tejada, P.V. Hendriksen, S.A. Sethi, *J. Magn. Magn. Mater.* **124**, 269 (1993).

[17] D.H. Martin, *Magnetism in Solids*, Iliffe Books, London 1967.

[18] E.F. Kneller, F.E. Luborsky, *J. Appl. Phys.* **34**, 656 (1963).

[19] A.J. Leggett, S. Chakravarty, A.T. Dorsey, M.P.A. Fisher, A. Garg, *Rev. Mod. Phys.* **59**, 1 (1987); A.J. Leggett, in: *Proc. Quantum Tunneling of Magnetism — QTM'94*, Eds. L. Gunther, B. Barbara, Kluwer Acad. Publ., The Netherlands 1995, p. 1.

[20] S. Arrhenius, *Z. Phys. Chem. (Leipzig)* **4**, 266 (1989).

[21] J. Tejada, X.X. Zhang, E.M. Chudnovsky, *Phys. Rev. B* **47**, 14977 (1993); J. Tejada, X.X. Zhang, in: *Proc. Quantum Tunneling of Magnetism — QTM'94*, Eds. L. Gunther, B. Barbara, Kluwer Acad. Publ., The Netherlands 1995, p. 121.