The Effect of Size, Shape and Environment on Magnetic Properties of a Nanoparticle: microscopic model analysis

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***Abstract* — Our theoretical study of magnetic nanoparticles is based on an original analytic approach, which allows to track down the intrinsic mechanisms of the observed magnetic properties. In particular, it reveals some misleading aspects of the standard phenomenological description of ferromagnetic nanoparticles. We show that quantum effects become important for particle size below 50 nm even at high temperatures. Several new results are relevant for controlling magnetization in nanostructures. Thus, the theory predicts that dividing a nanoparticle in two pieces may enhance and even generate a spontaneous magnetization. The effect grows nonlinearly with smaller size and is especially large for structures with anisotropic shape. Generally, at a given temperature and given number of atoms nanoparticles of a more isotropic shape have a larger polarization. However, coupling to environment strongly affects the magnetization: for a free-standing particle it is progressively suppressed for smaller sizes while for a particle with surface spins pinned by the coupling this trend is reversed. Due to this boundary induced polarization mechanism the Curie temperature T_c in the latter case may be several times larger. Moreover, anisotropic structures are much more sensitive to the environment than the isotropic ones: e.g., placing a free-standing nanorod into an appropriate environment may lead to an abrupt increase in its magnetization, which can be larger than that of a cubic particle of the same volume.**

***Index Terms* — boundary conditions, magnetic nanoparticles, shape anisotropy, size dependence, quantum effects.**

I. INTRODUCTION

Nanostructures continue to expand their application area and to attract a significant research effort, in particular in biomedical engineering [1]. To control their properties the technological development requires understanding of the inherent physical and chemical mechanisms. To this end a large variety of methods are being developed and used in an attempt to match the complexity of the "nano-world", as anticipated by R. Feynman in his famous 1959 talk at Caltech "There's plenty of room at the bottom". Aside from direct experiments, most of our knowledge of magnetic nanostructures comes from numerical simulations (so called "ab-intio" methods, exact cluster diagonalization etc.) and the phenomenological methods, which attempt to describe the observed behavior in terms of the well established "bulk" materials or a "macroscopic limit" [2]. Although the limitation to a fixed number of atoms accessible by numerical methods is ever less restrictive due to advances of computer science, one still needs a proper interpretation of the obtained data. This explains the need of analytical approaches, which have advanced much less however. The major stumbling block is namely the qualitatively higher complexity level separating the well studied "large system" limit from its "small" counterpart. We have addressed the issue of the temperature dependent magnetization of magnetic nanostructures by developing our earlier approach to exact solutions for the excitation spectra in finite crystals described, in this case, by the quantum Heisenberg spin lattice model, e.g. [3-5]. The thermodynamic quantities obtained in this way contain explicit dependences on all the parameters of the system and reveal their connection to the measured quantities.

II. DESCRIPTION OF THE APPROACH

The model describes a nanoparticle of rectangular shape consisting of $V=N \times N \times L$ magnetic ions with spin S in the nodes of a simple crystal lattice and coupled via nearest neighbor ferromagnetic exchange interaction J. On the surface of the particle the spins may be free or pinned by the coupling to the environment in which the particle is immersed or coated. These boundary conditions affect the spectrum of the main collective excitations, spin

waves, in the particle and have been discussed before [6]. One of these excitation modes plays a special role in a nanoparticle in contrast to bulk materials: the uniform rotation of the magnetization vector μ. For temperatures above certain value T_B there is no a preferential orientation of this vector so that the effective polarization μ_{eff} is virtually zero, while at lower temperatures the rotation is blocked by relatively weak anisotropy field of the crystal. It is necessary to separate this super-paramagnetic behavior from the excitations which reduce the magnitude of the intrinsic magnetization vector μ. The energy of these dispersive magnon excitations is essentially a cosine function of momentum *q*:

$$\varepsilon_{\mathbf{q}} = 2JS\hbar^2 \sum_{l=x,y,z} (1 - \cos q_l) \sim J\hbar^2 \sum_l (m_l/N_l)^2,$$

where the lattice spacing is set to *1* , $m_l = 1, 2, \ldots$ and N_l are either N or L. So, there is a minimal excitation gap when *N* and *L* are finite. Estimation of the thermal energy required to overcome this gap in the case of a cubic *Fe* nanoparticle gives the critical temperature $T^* = \hbar^2 JS/N^2$ which can reach 10-20 Kelvin. *T** is often thought to indicate the onset of the "quantum regime" when discreteness of the excitation spectrum becomes obvious indeed. However, from the low energy expression of the above dispersion it can be shown that this is precisely the temperature at which the de Broglie wavelength of the magnon becomes as large as the crystal size. The temperature dependence becomes trivial, excitations being virtually frozen out below *T** . It is then easy to understand that in fact the nontrivial quantum effects are important at temperatures much larger than *T** , when large number of atoms are still quantum correlated. Thus, detailed calculations which consider deviation from the classical Boltzmann distribution of magnons give an estimate for the onset temperature at about *0.5* T_c for nanoparticles of a few dozens of nm.

This temperature also marks the threshold of the low-temperature expansion we have developed by examining the exact quantum Bose-Einstein distribution with the fully discrete spectrum above. Magnetization is calculated as a quantum statistical average

$$\mu(T) = \mu(0)\left(1 - \frac{1}{VS}\sum_{\mathbf{q}\neq\mathbf{0}} [\exp(\beta\varepsilon_{\mathbf{q}}) - 1]^{-1}\right)$$

Depending on the chosen boundary conditions this leads to (e.g. For the free sample):

$$\mu(T)/\mu(0) = 1 - \sum_{m=1}^{\infty} \frac{1}{SV}\left(\prod_{l=x,y,z}\sum_{m_l=0}^{N_l-1} \exp\left[-4n\beta JS\sin^2\left(\frac{\pi m_l}{2N_l}\right)\right] - 1\right),$$

The discrete sums are then transformed into series of Bessel functions [7]. The generalized low temperature expansion is then constructed in terms of T/T_c << 1 and the new parameter $P = TN^2/4\pi JS > 1$. We give below the few terms of the final result for the case of a free-standing cubic nanoparticle

$$\mu(T)/\mu(0) \simeq 1 - BT^{3/2} - \frac{3T}{8\pi NJS^2}\ln\left(TN^2/\pi JS\right) - \frac{T}{10\pi NJS^2}, \qquad (1)$$

Where $B = \zeta(3/2)\, S^{-5/2}\,(4\pi J)^{-3/2}$ is the *bulk* value of the Bloch coefficient.

For an elongated shape of the sample, e.g. a rectangular nanorod, $V = N \times N \times L,\ L \geq N \gg 1$ and periodic boundary conditions the result is

$$\mu(T)/\mu(0) \simeq 1 - BT^{3/2} - \left(\frac{L/N - 3.9}{NS}\right)\frac{T}{4\pi JS} \qquad (2)$$

III. RESULTS AND DISCUSSION

Because of the explicit dependence on the parameters (size, shape, boundaries, temperature, coupling strength) in all the cases considered within our approach it is possible to establish their connection to the overall behavior of the system. In particular, it is clear from the above formulas that the bulk (Bloch) behavior is recovered when $N \to \infty$ without any change in the coupling constant. This conclusion contradicts the common opinion based on the phenomenological theory. Indeed, the standard approach in the analysis of experimental data is to fit them by the "generalized Bloch" formula:

$$\mu_{phen}(T) = \mu(0)(1 - \gamma T^{\alpha}). \qquad (3)$$

It was first introduced in the analysis of cluster numerical simulations as a purely descriptive tool required to fit the obtained data. The main argument in its qualitative justification is that as the magnetic properties on the surface of a particle are obviously different from its interior, one should observe a kind of an averaged behavior between the two. Since the surface to volume ratio is increasing for a smaller size, so should increase the deviation of the phenomenological parameters. Relying on the physical content of its macroscopic limit with α = 3/2 and the Bloch constant γ determined by the characteristics of the magnon spectrum, this analysis nevertheless fails to give a coherent explanation of the observed behavior. In particular, one could not find any regular pattern in the size dependence of α found to be both above and below the bulk value, while γ grows continuously for smaller particles. This would imply a large softening of the magnon excitations or a decrease of the coupling constant *J* in nanoparticles, e.g. [8]. Our approach, on the contrary, which takes explicit account of the surface states, leads to form of the "generalized Bloch law" rather different from Eq. (3). Moreover, we were able to reproduce the numerical cluster simulations equally well as the phenomenological formula. Therefore our results cast a serous doubt on the validity of the existing phenomenological description.

Another interesting observation is that the logarithmic terms demonstrate a rather slow convergence, meaning that deviations from bulk behavior may be observed in relatively large nanostructures. On the other hand, it is known from experimental works that one can observe values typical for the bulk material even in small nanoparticles. Our analysis shows that this may occur [illegible] of the shape anisotropy or of the effect of [illegible]ent on the surface spins of the sample. The latter includes coating or formation of a special layer on the

surface of the nanoparticle during the technological process. The first can be seen from Eq. (2), which shows that for a symmetric shape magnetization is always larger than in the bulk. Deformation of the symmetric (cubic) shape causes a decrease of magnetization which can reach the Bloch value (when L is about $4N$ in this case). To illustrate the effect of environment we show the expression for the case of a cubic particle with all spins on its surface pinned:

$$\mu(T)/\mu(0) \simeq 1 - BT^{3/2} + \left(\frac{0.12T}{JNS^2}\right)\ln\left(TN^2/\pi JS\right) \quad (4)$$

It can then be seen from Eqs. (1) and (4) that magnetization for these two "extreme" boundary conditions deviates from the Bloch result in an opposite sense. It is therefore natural to expect that for an "intermediate" case of an incomplete pinning it can be close to the Bloch result.

Figs.1 and 2 also demonstrate a qualitatively opposite size dependence of magnetization for the two boundary conditions mentioned above. If decreasing the size of a free particle diminishes the overall magnetization due to enhanced fluctuations, for a surface-pinned case magnetization starts to rapidly increase at about 10^4 atoms.

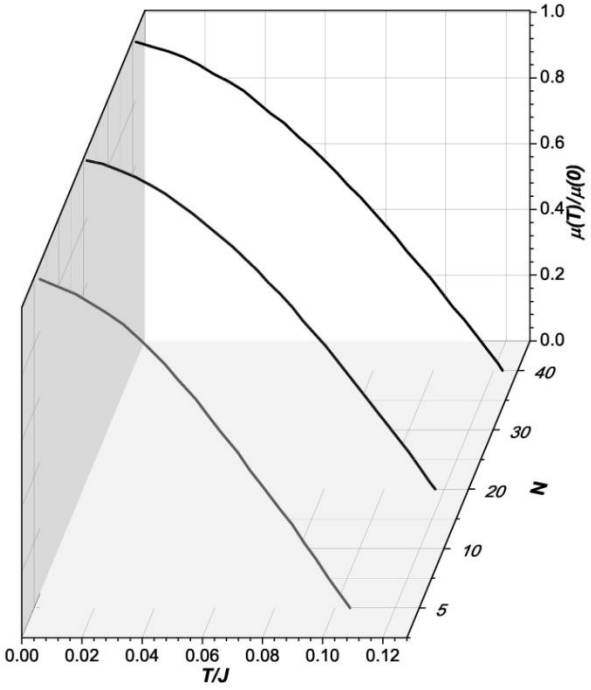

Fig. 1. Size and temperature dependent magnetization of a cubic free-standing particle composed of N^3 atoms with spin 1/2.

Note that the Curie temperature at this point is almost twice that of a free standing particle and if the latter is placed in the respective environment its magnetization would jump to about 0.84 of the saturation value. The same abrupt increase of magnetization would take place if the sample is divided in two pieces, as can be inferred from these figures. Moreover, the effect is much stronger for anisotropic shapes, as can be seen from the Figs 3 and 4, illustrating their sensitivity to boundary conditions.

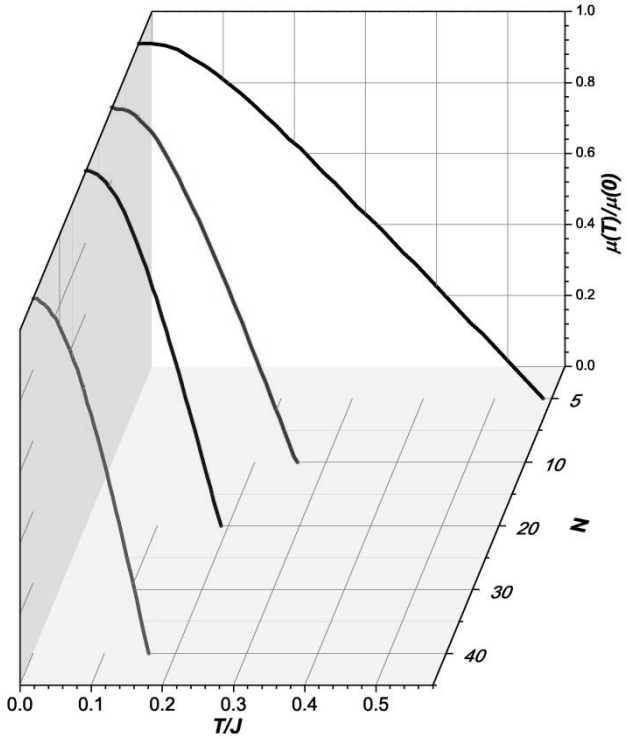

Fig. 2. Size and temperature dependent magnetization of a cubic nanoparticle embedded in a surface-pinning environment and composed of N^3 atoms with spin 1/2.

Taking as an example the elongated geometry of a rectangular nanorod or nanowire we find a remarkably large difference of the Curie temperatures for the pinned and free boundary conditions, which can reach over an order of magnitude. Even for samples of up to several thousands of atoms (a number typical for magnetic Co nanograins in computer hard disks) the difference actually increases with the size of the nanoparticle. A similar result is obtained for other shape anisotropies relevant for applications.

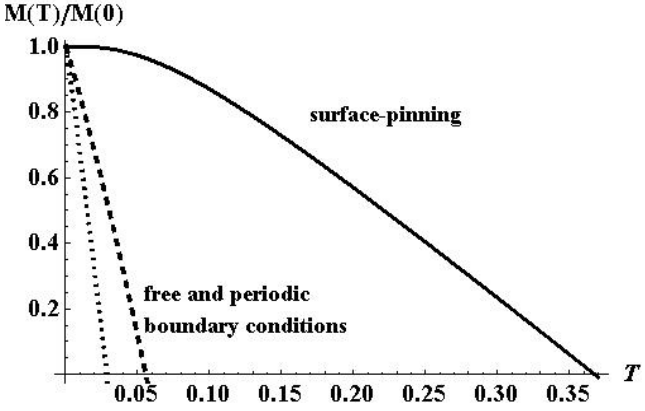

Fig. 3. Temperature dependent magnetization of the shape anisotropic structure (rectangular nanorod) embedded in a surface-pinning environment, free (the dotted curve) and periodic (dashed) boundary conditions. The number of S=1/2 spins is N x N x L=5 x 5 x 100.

This difference arises from the strong suppression with size of the magnetization in a free-standing anisotropic particle compared to the one placed in a pinning environment. The physical mechanism of such a contrast

is the balance between the enhanced spin fluctuations in anisotropic quasi one- or two-dimensional structures and the inhibiting effect of the coupling to the environment on the fluctuations destroying the long range order. Note that the Curie temperature in Fig. 4 is larger than the that of cubic sample of the same volume in Fig. 2.

Another important result of our theory is that it explains the visibly quasilinear temperature dependence of magnetization observed in many experiments on nanostructures in terms of size, shape and boundary conditions. This kind of

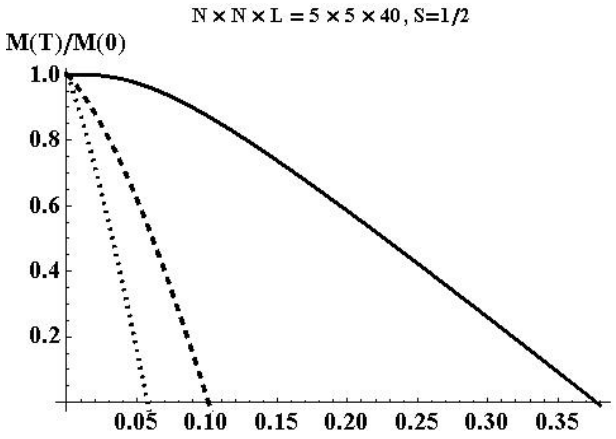

Fig. 4. The same as in Fig. 3, but for a shorter nanorod containing the same number of atoms as in the cubic sample of Fig. 2 (red line).

deviation from the Bloch law is presently ascribed to the excitations of the uniform magnetic mode mentioned earlier [9] and totally ignores the whole spectrum of excitations, as included in our approach. As can be seen both in experiment and in our results the quasilinear dependence is present at sufficiently large temperatures, where all the modes are actually excited and we therefore believe this is the only reliable mechanism of the quasilinear behavior.

IV. CONCLUSION

We have outlined the main elements of the new analytic approach to the description of magnetization in ferromagnetic nanostructures. It is based on the quantum Heisenberg model with spin exchange type of coupling, which, as we argue, captures the main physical features of the nanostructures below *50* nm in size. In this case quantum effects and discreteness of the excitation spectrum are shown to be relevant even at large temperatures and not just at low *T* as is common to think. The approach has allowed to critically reconsider the basics of the existing phenomenological description, in particular the functional form of the assumed temperature dependence of the "generalized" Bloch law. It should be emphasized that shape, size and boundary dependences are totally absent in the standard phenomenological analysis. This explains the irregular variation of the values of fitting parameters extracted from different measurements. In contrast, these dependences are considered explicitly in our theory and have been calculated for a number of specific examples. The results agree well also with the numerical cluster simulations. Several properties revealed by the theory may be relevant for applications of magnetic nanoparticles. Thus, generally, at a given temperature and given number of atoms nanoparticles of a more isotropic shape have a larger polarization. However, coupling to environment can strongly modify the magnetization: for a free-standing particle it is progressively suppressed for smaller sizes while for a particle with surface spins pinned by the coupling this trend is reversed. Thus we have shown that in the latter case the magnetic nanorod has an unexpectedly higher magnetization than a symmetric nanoparticle of the same volume. In other words, anisotropic structures are much more sensitive to the environment than the isotropic ones. One of the implications is that placing a free-standing nanorod into an appropriate environment may lead to an abrupt increase in its magnetization, an effect which may be used, e.g. In applications in sensor devices.

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