Some characteristic behaviours of a spin-1/2 Ising nanoparticle

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Abstract. By using the effective-field theory with correlations based on the probability distribution technique; the magnetization, susceptibility, internal energy, specific heat and the free energy expressions for a ferromagnetic spin-1/2 Ising nanoparticle have been developed and calculated numerically for different surface shell exchange coupling parameter. A number of interesting phenomena have been observed, depending on the surface shell exchange coupling term.

1. Introduction
Magnetic nanoparticle (NP) systems have been receiving considerable attention in the last 15 years from both experimental and theoretical researchers [1, 2]. This is motivated by numerous possibilities of their applications in permanent magnets, recording media, microwave absorption, and in biomedical applications [3]. Furthermore, these NPs show excellent new properties which are totally different from those observed in the bulk counterparts, such as superparamagnetism, high field irreversibility, high saturation field, extra anisotropy contributions or shifted loops after field cooling [4, 5], because the NPs are greatly affected by the particle size [6].

From the theoretical point of view, these systems have been studied by a variety of techniques such as mean-field theory (MFT) [7], effective-field theory (EFT) with correlations [8, 9], Green Functions (GFs) formalism [10], and Monte Carlo (MC) simulations [11, 12]. By using the EFT with correlations, the magnetic and the thermodynamic properties of several magnetic NPs have been studied by different theoretical researchers. For instance, Canko et al. [13] have investigated the effect of crystal field on the magnetization, magnetic susceptibility, specific heat, internal energy, specific heat and the free energy of a Blume-Capel Ising nanotube. The authors found that the system undergoes first- and second- order phase transitions. The same results were found by Kantar et al. [14], by studying the thermodynamic and magnetic properties of ternary mixed Ising NPs with core/shell structure. Similarly, Şarlı [15] has investigated the temperature dependencies of the
magnetic properties of the both ferromagnetic and the antiferromagnetic cylindrical mixed spin-1/2 core and spin-1 shell Ising nanotube system. The author found that the nanotube system undergoes a first-order phase transition for the weak surface/shell exchange interaction. However, it undergoes only a second-order phase transition for the strong interaction. Moreover, Kantar et al. study [16] on the thermal variation of magnetization of the mixed spin-1/2 core and spin-3/2 shell Ising NPs, with a crystal field interaction show that this system exhibits just a second-order phase transition as it is proved by the free energy of the system, and they have also found one or two compensation points in the magnetization curves. However, only one compensation point has been found by Kocakaplan et al. [17] in the thermal variations of the total magnetization of the spin-1/2 hexagonal Ising nanowire system with core/shell structure. Recently, in our work [18, 19], we have investigated the effect of the exchange interaction between core and surface shell spins on the thermodynamic and the magnetic properties of a transverse antiferromagnetic Ising NPs. We have found a number of interesting phenomena, such as the existence of the compensation points. In addition, two and even three compensation points have been found in the magnetization curves of a double-wall cubic metal nanotube by Liang et al. [20], which are not predicted in the Néel theory [21]. They have also observed a discontinuity at transition temperature in all the initial susceptibility curves. The purpose of this work is to investigate the effect of the surface shell exchange coupling on the magnetic and thermodynamic properties of a ferromagnetic Ising nanocube. For this aim, we have organized this paper as follows: In Section 2, we outline the formalism. In Section 3, we present the results and discussion, and finally we give a brief conclusion in Section 4.

2. Model and formalism
We consider a $5 \times 5 \times 5$ ferromagnetic cubic NP composed of a ferromagnetic spin-1/2 core which is interacting with a ferromagnetic spin-1/2 surface shell as depicted in the figure below (figure 1).

![Figure 1: Schematic representation of magnetic spins in a cubic nanoparticle. Solid, dotted, and dashed lines represent the exchange interactions of the surface shell, core, and interface, respectively. The spin holders at the surface sites are denoted by $S_1, S_2, S_3, S_4, S_5$ and $S_6$, whereas $C_1, C_2, C_3$ and $C_4$ define the spin holders in the core site.](image-url)
The inner spins are called the core (c) region which is surrounded by the outer spins that are known as the surface shell (s) of the particle. The number of core spins is $N_c = 27$ and the number of surface shell spins is $N_s = 98$. The Hamiltonian of the system is expressed as follows:

$$ H = -J_s \sum_{\langle ij \rangle} \sigma_i^z \sigma_j^z - J_c \sum_{\langle nm \rangle} \sigma_n^z \sigma_m^z - J_{cs} \sum_{\langle im \rangle} \sigma_i^z \sigma_m^z, \quad (1) $$

where $\sigma_i^z$ denotes the $z$ component of a quantum spin operator $\sigma$ of magnitude $\sigma = 1/2$ at the site $i$. $J_s$, $J_c$ and $J_{cs}$ are the exchange interactions between the nearest-neighbour magnetic spins in the surface shell, the core and between the core and the surface shell interface ($J_{cs} > 0$) of the nanocube, respectively.

The theory to be used is the EFT in which the attention is focused on the cluster comprising just a single selected spin and the neighbouring spins with which it directly interacts. To this end, the Hamiltonian is split into two parts

$$ H = H' + H_i. \quad (2) $$

The first term denoted by $H'$ does not depend on the site $i$, while the second term ($H_i$) includes all contributions associated with the site $i$:

$$ H_i = - (\sum_j J_{ij}) \sigma_i^z. \quad (3) $$

The term $J_{ij}$ represents the strength of the exchange interaction between the spins at nearest-neighbour sites $i$ and $j$, where $i$ is the single selected spin and $j$ represents the neighbouring spins with which it directly interacts.

![Figure 2: Reduced temperature dependence of the total magnetization of the system for some selected values of the surface shell exchange coupling $r_s$ ($r_s = 0.1, 0.2, 0.3$ and $0.4$), with $r_{cs} = 0.01$.](image)

Using the approximation introduced by Sá Barreto et al. [22] we obtain the identity

$$ \langle \sigma_i^z \rangle = \frac{Tr[\sigma_i^z e^{-\beta H_i}]}{Tr[ e^{-\beta H_i}]], \quad (4) $$
where the angular bracket $<...>$ denotes the canonical thermal average, $\beta = \left(k_B T \right)^{-1}$ with $k_B$ stands for the Boltzmann constant and $T$ is the temperature. If the exchange interactions were restricted only to the nearest-neighbours, and using the EFT with a probability distribution technique [23], the longitudinal magnetization of the system would be given by

$$m_z^i = \left< \sigma_z^i \right> = \left< f_z \left( \sum_j J_{ij} \sigma_j^z \right) \right>,$$

with

$$f_z(\sum J_{ij} \sigma_i^z) = \frac{1}{2} \tanh\left( \frac{\beta}{2} \sum J_{ij} \sigma_i^z \right).$$

To perform the thermal averaging on the right-hand side of equation (5), we follow the general approach described in reference [23]. First of all, in the spirit of the EFT, multispin-correlation functions are approximated by products of single spin averages. We then take advantage of the integral representation of the Dirac's delta distribution in order to write equation (5) in the following form

$$m_z^i = \int dy f_z(y) \frac{1}{2\pi} \int d\lambda \exp(i\lambda \lambda) \prod \left< \exp(i\lambda J_{ij} \sigma_j^z) \right>$$

Figure 3: Reduced temperature dependence of the total susceptibility of the system for some selected values of the surface shell exchange coupling $r_s$ ($r_s = 0.1, 0.2, 0.3$ and $0.4$), with $r_{cs} = 0.01$.

In the calculation of equation (7), the commonly used approximation has been made according to which the multi-spin correlation functions are decoupled into products of the spin average. To make progress, we introduce the probability distribution of the spin variable $\sigma_j^z$:

$$P(\sigma_j^z) = \frac{1}{2} [(1-2m_j^z)\delta(\sigma_j^z + \frac{1}{2}) + (1+2m_j^z)\delta(\sigma_j^z - \frac{1}{2})]$$

(8)
The explicit formulation of magnetizations has been given in reference [32]. The total longitudinal magnetization per site is given by

\[ M_T = \frac{1}{125} (98M_s + 27M_c) \]  

(9)

where \(M_s\) and \(M_c\) represent respectively the longitudinal magnetization of surface shell and core of the nanocube, which are given by

\[ M_c = \frac{1}{27} (8m_{c_1}^z + 12m_{c_2}^z + 6m_{c_3}^z + m_{c_4}^z) \]  

(10)

and

\[ M_s = \frac{1}{98} (8m_{s_1}^z + 24m_{s_2}^z + 12m_{s_3}^z + 24m_{s_4}^z + 24m_{s_5}^z + 6m_{s_6}^z) \]  

(11)

It is also interesting to study the behaviour of the longitudinal susceptibility of each site of the nanocube, which is defined by

\[ \chi = \frac{1}{125} (98\chi_c + 27\chi_s) \]  

(12)

where the core and the surface shell susceptibilities are given by

\[ \chi_c = \frac{1}{27} (8\chi_{c_1}^z + 12\chi_{c_2}^z + 6\chi_{c_3}^z + \chi_{c_4}^z) \]  

(13)

and

\[ \chi_s = \frac{1}{98} (8\chi_{s_1}^z + 24\chi_{s_2}^z + 12\chi_{s_3}^z + 24\chi_{s_4}^z + 24\chi_{s_5}^z + 6\chi_{s_6}^z) \]  

(14)
The details of calculus of the each site of the longitudinal susceptibility have been given in reference [32].

By using the approximated spin correlation identities introduced by Sá Barreto et al. [24]

\[
\langle f_i \sigma_j^z \rangle = \left\langle f_i \frac{Tr[\sigma_i^z e^{iH}]}{Tr[e^{iH}]} \right\rangle,
\]

we can easily obtain the internal energy \( U \) of the system from the thermodynamic average of the Hamiltonian, as it has done by Kaneyoshi et al. [25] in the mixed-spin system

\[
U = \langle H \rangle = -\frac{1}{2} \left( \frac{1}{128} \left( 8 \langle u_i^z \rangle + 12 \langle u_s^z \rangle + 6 \langle u_s^z \rangle \right) \right)
+ 8 \langle u_i^z \rangle + 24 \langle u_s^z \rangle + 12 \langle u_s^z \rangle + 24 \langle u_s^z \rangle + 24 \langle u_s^z \rangle + 24 \langle u_s^z \rangle
\]

where

\[
\langle u_i^z \rangle = \left\langle \sum_j J_{ij} \sigma_j^z f_z \left( \sum_j J_{ij} \sigma_j^z \right) \right\rangle.
\]

![Figure 5. Reduced temperature dependence of the internal energy of the system for some selected values of the surface shell exchange coupling \( r_s \) \((r_s = 0.1, 0.2, 0.3 \text{ and } 0.4)\), with \( r_{cs} = 0.01 \).](image)

The specific heat of the system is obtained from the relation:

\[
C_h = \frac{\partial U}{\partial T}
\]

The free energy of the system is defined as:

\[
F = U - T \int_0^\infty \frac{C_h}{T} dT
\]

By solving all these equations numerically, we can easily obtain the magnetic and the thermodynamic properties of the surface/shell nanocube system.
3. Numerical results and discussion

In this section, we investigate the effect of the surface shell exchange coupling \( r_s \) on the magnetic and thermodynamic properties of a ferromagnetic spin-1/2 Ising nanocube. In the following discussion, we take \( J_c \) as a unit of the energy and we define the reduced exchange interactions as \( r_{cs} = J_{cs}/J_c \) and \( r_s = J_s/J_c \).

The effect of the surface shell exchange coupling on the magnetic and thermodynamic properties of the particle is examined in figures 2, 3, 4, 5 and 7 for some selected values of \( r_s \) (\( r_s = 0.1, 0.2, 0.3 \) and 0.4), and with a fixed value of \( r_{cs} = 0.01 \). Figure 2 shows the total magnetization versus reduced temperature \((k_B T/J_c)\). As seen from this figure, all the magnetizations are 1.0 at zero temperature, then they suddenly decrease at the reduced temperatures: \( k_B T/J_c = 0.322, 0.629, 0.935 \) and 1.24 when \( r_s = 0.1, 0.2, 0.3 \) and 0.4, respectively and become zero at the same critical temperature: \( k_B T_c/J_c = 3.286 \). Therefore, a second-order phase transition occurs at this critical temperature and the phase transition is from the ferromagnetic phase to the paramagnetic one. The shape of the magnetization curves is S-type behaviour which is not predicted in the Néel nomenclature [21]. This shape is also found theoretically in references [16, 17; 26-31]. Figure 3 shows the temperature dependence of the total susceptibility \( \chi_T \), for some selected values of \( r_s \). Two distinct peaks appear in these curves for each value of \( r_s \) as seen in this figure. The first one which has a sharp shape corresponds to the fluctuation of the magnetization curves, whereas the second one emerges at the critical temperature. Figure 4 illustrates the thermal variation of the core and surface shell magnetizations for the same parameters as those in the above figures. In this figure, \( M_c = M_s = 1.0 \) at zero temperature. In addition, with increasing temperature the \( M_c \) curves show a monotonic decrease exhibiting the Q-type behaviour [21] which indicate that \( r_s \) does not have any considerable effect on the core magnetization, whereas \( M_s \) curves take several magnitudes in depending on \( r_s \) values which indicate that \( r_s \) has an apparent effect on the thermal variation of the surface shell magnetization. These results indicate that the main contribution of the total magnetization behaviour is the surface shell magnetization of the particle as it is found in our previous work of an antiferromagnetic transverse spin-1/2 Ising nanocube [32]. Figure 5 shows the effect of \( r_s \) on the internal energy. One can see that, the internal energy curves have a

Figure 6. Reduced temperature dependence of the specific heat of the system for some selected values of the surface shell exchange coupling \( r_s \) \((r_s = 0.1, 0.2, 0.3 \text{ and } 0.4)\), with \( r_{cs} = 0.01 \).
fluctuation at the reduced temperatures: 0.322, 0.629, 0.935 and 1.24 when \( r_s = 0.1, 0.2, 0.3 \) and 0.4, respectively, and represent a discontinuity of the curvature at the critical temperatures. In addition, for any fixed value of \( k_B T/J_c \), the stronger surface shell exchange coupling makes internal energy \( U \) decreasing. The specific heat-reduced temperature is plotted in figure 6. It is clearly seen that the \( C_h \) profile undergoes a sharp drop at the critical temperature after the change of the curvature at the fluctuation of the magnetization curves. The same profile is also observed in the specific heat curve of the spin- \( \frac{1}{2} \) Blume-Capel model [33]. In figure 7 we plot the numerical results of free energy of the system for the same parameters in previous figures. We note from this figure that the system presents only a second order phase transition because the free energy curves do not exhibit a discontinuous behaviour at the critical temperature. We can also notice that the free energy is equal to the internal energy at the ground state.

![Figure 7. Reduced temperature dependence of the free energy of the system for some selected values of the surface shell exchange coupling \( r_s \) \((r_s = 0.1, 0.2, 0.3 \) and 0.4\), with \( r_{cs} = 0.01 \).](image)

In order to investigate the effect of \( r_s \) on the critical temperature of the system, we have plotted the phase diagram \((k_B T/J_c, r_s)\) in figure 8. It is clearly seen from this figure that, when \( r_s \) is less than 1.07 the critical temperature remains almost constant for all value of \( r_s \), whereas, for \( r_s > 1.07 \) it increases linearly. The same behaviour is observed in a ferromagnetic cylindrical Ising nanowire [34].
Conclusion
In this work, we have studied the thermodynamic and magnetic properties of a ferromagnetic nanocubic particle by employing the EFT based on the probability distribution technique with correlations. It is found that the surface shell exchange coupling $r_s$ has a strong effect on the behaviour of the magnetization, internal energy, specific heat and free energy of the system.

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Figure 8. Phase diagram of the system in ($k_B T_c / J_c - r_s$) plane for $r_{cs} = 0.01$. 
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