Non-equilibrium dynamics of a ferrimagnetic core–shell nanocubic particle

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Abstract

The non-equilibrium dynamics of a single cubic core–shell ferrimagnetic nanoparticle system under a time dependent oscillating magnetic field is elucidated by making use of a classical Monte Carlo simulation technique with a standard Metropolis algorithm. Many interesting and unusual thermal and magnetic behaviors are observed, for instance, the locations of dynamic phase transition points change significantly depending upon amplitude and period of the external magnetic field as well as other Hamiltonian parameters in related planes. Much effort has also been devoted to the influences of the varying shell thickness on the thermal and magnetic properties of the particle, and outstanding physical findings are reported in order to better understand the dynamic process of the studied nanoparticle system.

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1. Introduction

With the reduction of the physical size of a magnetic system to a characteristic length, the surface to volume ratio increases. As a result of this process, the thermal and magnetic properties of the system begin to sensitively depend on the size which is different from those observed in the bulk material. Influences of finite-size originating from the nanometric size of particle and surface effects due to the symmetry breaking of the crystal structure of the particle on the magnetic properties of magnetic nanoparticles have provided a conspicuous and productive field for the interaction between theoretical works [1] and technological [2–4] as well as biomedical applications [5–8]. On the theoretical picture, equilibrium properties of a great number of nanoparticle systems have been studied by employing some of the well defined physical methods such as molecular field approximation (MFA) [9–12], effective field theory (EFT) [12–14], Monte Carlo (MC) simulations [9,10,15–20] and Green function formalism [21,22]. From the experimental point of view, it is possible to mention that due to the recent developments in chemical synthesis techniques scientists are able to produce various types of controllable nanoscaled materials...
such as nanowires, nanotubes, nanorods, nanocubes as well as other more complex shapes [23–32] and they have many applications in different types of nanotechnology areas [33,34]. For example in Ref. [30], a closed-form theory for the investigation of smallest diameter of metallic nanorods has been formulated by benefiting from physical vapor deposition. Moreover, the results obtained from the theory have been verified by making use of lattice kinetic Monte-Carlo simulation technique.

The statistical mechanics of non-equilibrium systems is a less developed and understood field of study than that for equilibrium systems. It is a fact that a magnetically interacting system under the influence of a time dependent oscillating magnetic field exhibits two important striking phenomena: Non-equilibrium phase transitions and dynamic hysteresis behavior. Nowadays, these types of non-equilibrium systems are in the center of scientists’ attention because they have exotic, unusual and interesting behaviors. For example, the universality classes of the Ising model and its variations under a time dependent driving field are different from its equilibrium counterparts [35–37]. It is possible to emphasize that non-equilibrium phase transitions originate due to a competition between time scales of the relaxation time of the system and oscillating period of the external applied field. To our knowledge, for the high temperatures and high amplitudes of the periodically varying magnetic field, the system exists in a dynamically disordered phase where the time dependent magnetization is able to follow the external applied magnetic field with some delay whereas this is not the case for low temperatures and small magnetic field amplitudes. The physical mechanism described above points out the existence a dynamic phase transition [35,38,39]. Apart from the investigation of dynamic properties of infinite size systems, there exists another research area attracting attention both experimentally and theoretically. This area is the examination and determination of the physical and magnetic properties of nanoparticles under the influence of an alternating magnetic field. At this point, it is beneficial to talk briefly about their well known features. For example, when magnetic nanoparticles are subjected to a periodically varying time-dependent magnetic field, the particles may not respond to the external magnetic field instantaneously, which causes interesting behaviors due to the competing time scales of the relaxation behavior of the particles and periodic external magnetic field. The aforementioned situations may give rise to the existence of heating effects related to losses during the magnetization reversal process of the particles. By means of the above discussed properties, the suspensions including suitable magnetic nanoparticles have received intense focus for cancer treatment with magnetic hyperthermia. It has been reported by the previously published studies in the literature that the efficiencies of nanoparticles leading to a heating process sensitively depend on the frequency and amplitude of the external applied field as well as the other particle features [40,41]. In this regard, the experimental and theoretical works concerning the physical investigation of nanoparticles under a time dependent magnetic field have a particularly important role in creating a better understanding of the mechanism underlying these types of systems.

On the other hand, we learned from theoretical studies mentioned below that clarification of thermal and magnetic properties of different shaped magnetic nanoparticle systems under the time dependent oscillating forcing field is possible by making use of well defined non-equilibrium statistical mechanical tools. For example, in Refs. [42,43], thermal variations of time averaged magnetizations, dynamic correlations between time dependent magnetic field and magnetization and hysteresis loop areas of cylindrical Ising nanowire and nanotube systems have been elucidated by benefiting from a Glauber type stochastic process [44], and it is reported that depending on Hamiltonian parameters, the considered systems exhibit different types of magnetization profiles, according to the Néel theory of ferrimagnetism [45,46]. Moreover, a comprehensive MC simulation study with standard Metropolis algorithm has been carried out to determine the dynamic phase transitions, hysteretic as well as finite size properties of a single ferrimagnetic nanocubic system with a core–shell structure, and a number of interesting and unusual behaviors are observed such as in the presence of ultrafast switching fields, the particle may exhibit a dynamic phase transition from paramagnetic to a dynamically ordered phase with increasing ferromagnetic shell thickness [47]. Very recently, a spherical core–shell nanoparticle system with a spin-3/2 core surrounded by a spin-1 shell layer with antiferromagnetic interface coupling is exposed to a sinusoidal magnetic field and it is found that dynamic phase boundaries strongly depend on the Hamiltonian parameters such as for the high amplitude and period values of the external field, the phase transition temperature sharply changes whereas it tends to slowly alter as the reduced magnitude of interlayer parameter increases. Moreover, it is observed that the magnetization curves of the particle have been found to obey P-type, N-type and Q-type classification schemes under certain conditions [48].

It is clear from the previously published works discussed above that equilibrium phase transition properties of different types of nanoparticle systems are clearly indicated, whereas non-equilibrium counterparts deserve a particular attention. From this point of view, a cubic nanoparticle composed of a spin-1/2 ferromagnetic core which is surrounded by a spin-1 ferromagnetic shell layer under the influence of a time dependent driving magnetic field is selected to determine the influences of the internal and external parameters as well as particle size on the dynamic phase transition properties of the cubic core–shell nanoparticle system. The main motivation of the present paper is to attempt to clarify the physical facts underlying these points. For this purpose, the outline of the paper is as follows: in Section 2 we briefly present our model. The results and discussion are presented in Section 3, and finally Section 4 contains our conclusions.

2. Formulation

A single cubic ferrimagnetic nanoparticle made of a spin-1/2 ferromagnetic core which is surrounded by a spin-1 ferromagnetic shell layer is considered. At the interface, an antiferromagnetic interaction between core and shell spins is defined. The particle is subjected to a time varying sinusoidal magnetic field. The Hamiltonian describing our model of the
magnetic system can be written as

$$\mathcal{H} = -J_{\text{int}} \sum_{\langle i, k \rangle} \sigma_i S_k - J_c \sum_{\langle i, j \rangle} \sigma_i \sigma_j - J_{\text{sh}} \sum_{\langle i \rangle} S_i S_j - h(t) \left( \sum_{i} \sigma_i + \sum_{k} S_k \right),$$

(1)

where $\sigma = \pm 1/2$ and $S = \pm 1$, 0 are spin variables in the core and shell sublattices. $J_{\text{int}}, J_c$ and $J_{\text{sh}}$ describe antiferromagnetic interface, ferromagnetic core and shell exchange interactions, respectively. $h(t) = h_0 \sin(\omega t)$ represents the oscillating magnetic field, where $h_0$ and $\omega$ are the amplitude and the angular frequency of the applied field, respectively. The period of the oscillating magnetic field is given by $\tau = 2\pi / \omega$. (...) denotes the nearest neighbor interactions on the lattice. We note that the value of the core exchange interaction $J_c$ is fixed to unity, and we use the normalized applied field amplitude $h = h_0/J_c$. We also set $k_B = 1$.

We will not give the simulation details in this work, they can be found in Ref. [47]. Data were generated over 20 independent sample realizations by running the simulations for 30 000 Monte Carlo steps per site after discarding the first 10 000 steps. This amount of transient steps is found to be sufficient for thermalization for the whole range of the parameter sets. Error bars are calculated by using the jackknife method [49].

For the studied system under the influence of a time dependent forcing field, instantaneous values of the sublattice magnetizations $M_c$ and $M_{\text{sh}}$, and the total magnetization $M$ at the time $t$ can be written as follows:

$$M_c = \frac{1}{N_c} \sum_{i=1}^{N_c} \sigma_i(t), \quad M_{\text{sh}} = \frac{1}{N_{\text{sh}}} \sum_{i=1}^{N_{\text{sh}}} S_i(t), \quad M_t = \frac{N_c M_c + N_{\text{sh}} M_{\text{sh}}}{N_c + N_{\text{sh}}},$$

(2)

here $N_c$ and $N_{\text{sh}}$ denote the number of spins in core and shell layers, respectively. At this point, it is beneficial to indicate that we select the number of core and shell spins as $N_c = 11^3$ and $N_{\text{sh}} = 15^3 - 11^3$ from Fig. 1 to Fig. 4 and in Fig. 6(a)–(b), respectively. From the instantaneous magnetizations, we obtain the dynamic order parameters (DOPs) as follows:

$$Q_c = \frac{1}{\tau} \oint M_c(t) dt, \quad Q_{\text{sh}} = \frac{1}{\tau} \oint M_{\text{sh}}(t) dt, \quad Q = \frac{1}{\tau} \oint M_t(t) dt,$$

(3)

where $Q_c, Q_{\text{sh}}$ and $Q$ denote the DOPs corresponding to the core and shell sublattices, and the overall lattice, respectively. We also calculate the time average of the total energy of the particle including both cooperative and field parts over a full cycle of the magnetic field as follows [50]:

$$E_{\text{tot}} = \frac{1}{\tau (N_c + N_{\text{sh}})} \oint \mathcal{H} dt.$$

(4)

Thus, the specific heat of the system is defined as

$$C = \frac{dE_{\text{tot}}}{dT},$$

(5)

where $T$ represents the temperature. Moreover, in order to take account the number of spin weight of core and shell, we also define two additional order parameters belonging to core and shell layers of the particle as follows:

$$O_c = \frac{N_c}{N_c + N_{\text{sh}}} Q_c, \quad O_{\text{sh}} = \frac{N_{\text{sh}}}{N_c + N_{\text{sh}}} Q_{\text{sh}}.$$

(6)

3. Results and discussion

In this section, we will touch upon the dynamic phase transition properties of a core–shell cubic nanoparticle system under a time dependent sinusoidal magnetic field source. We will discuss how the applied field amplitude and period as well as other Hamiltonian parameters affect the stationary state behavior of the particle and will focus our attention on what kind of physical relationships exist between thermal and magnetic properties of the particle and system size.

In order to elucidate the influences of the antiferromagnetic interface coupling parameter on the dynamic evolution of the cubic nanoparticle system, we give the dynamic phase boundaries of the particle in the $(J_{\text{int}}/J_c - T_c/J_c)$ planes for values of $J_{\text{sh}}/J_c = 0.5$ with some selected values of amplitude ($h = 0.0, 0.25, 0.5$), and three considered periods ($\tau = 50, 100, 200$) of the applied field in Fig. 1(a)–(c). It is obvious from the figures that the dynamic phase transition point increases when the strength of the antiferromagnetic interface coupling $J_{\text{int}}/J_c$ increases. Actually, these are expected results because when the absolute value of $J_{\text{int}}/J_c$ is increased it becomes dominant against the periodic local fields and the nanoparticle exhibits a strong dynamically ordered phase. Therefore, a relatively large amount of thermal energy is needed to observe a dynamic phase transition in the system. Another important finding is that as the applied field amplitude increases the phase boundary deviates from its equilibrium boundary. The physical mechanism underlying this observation can be explained as follows: If one keeps the system in one well of a Landau type double well potential, a certain amount of energy originating from magnetic field is necessary to achieve a dynamic symmetry breaking. If the amplitude of the applied field is less than the
Fig. 1. (Color online) Dynamic phase boundaries of a cubic nanoparticle system in the $(J_{\text{int}}/J_c - T_c/J_c)$ planes for value of $J_{sh}/J_c = 0.5$ with some selected values of applied field amplitude $h = 0.0, 0.25$ and $0.5$. The curves are plotted for three values of oscillation period: (a) $\tau = 50$, (b) $\tau = 100$ and (c) $\tau = 200$.

Fig. 2. (Color online) Effects of the antiferromagnetic interface coupling parameter on the total (a) and core–shell magnetizations (b) of a cubic nanoparticle system corresponding the phase diagrams illustrated in Fig. 1(b) with selected amplitude $h = 0.25$ and period $\tau = 100$ values of the external magnetic field.

required amount then the system oscillates in one well. In this situation, the magnetization does not change its sign. In other words, the system oscillates around a nonzero value. This region is a dynamically ordered phase. When the temperature increases, the height of the barrier between the two wells decreases. As a result of this, less magnetic field is necessary to push the system from one well to another and hence the magnetization can change its sign for this amount of field. Consequently, the time averaged magnetization over a full cycle of the oscillating field becomes zero.

The antiferromagnetic interface coupling parameter dependencies of the total and core–shell dynamic order parameters are shown in Fig. 2(a)–(b) corresponding to the dynamic phase diagram plotted in Fig. 1(b) with a value of $h = 0.25$. It is clear from the Fig. 2(a) that the total magnetization gradually decreases from starting its saturation value with increasing thermal agitation, and the studied system exhibits a second order phase transition at the critical temperature. The aforementioned situation is valid for considered $J_{\text{int}}/J_c$ values. As we mentioned before in detail, the location of dynamic phase transition point changes depending on the $J_{\text{int}}/J_c$ value. We also note that for the considered Hamiltonian parameters the system displays a second order phase transition. On the other hand, it can be easily seen from the Fig. 2(b) that even though the ferromagnetic exchange coupling of the core particles is greater than that of shell layer, both core and shell layers of the particle bring about a dynamic phase transition at the same critical temperature which is a result of the relatively strong interface coupling parameter.
Fig. 3. (Color online) Equations of the applied field amplitude on the total (a) and core–shell magnetizations (b) of a cubic nanoparticle system corresponding to the phase diagrams illustrated in Fig. 1(b) with selected antiferromagnetic interface coupling parameter $J_{\text{int}}/J_c = -0.5$ and applied field period $\tau = 100$ values.

Fig. 4. (Color online) (a) Dynamic phase boundaries of a cubic nanoparticle system in the $(J_{\text{int}}/J_c - T_c/J_c)$ planes for values of $J_{\text{sh}}/J_c = 0.5$ at various applied field periods $\tau = 50, 100$ and 200. (b) The influences of the applied field period on the thermal variations of core and shell magnetizations of the particle for $J_{\text{int}}/J_c = -3.0, J_{\text{sh}}/J_c = 0.5, h = 0.5$, and $\tau = 50, 100$ and 200.

Fig. 3(a)–(b) illustrates the effects of the applied field amplitude on the total and core–shell magnetizations of the particle corresponding to a dynamic phase diagram depicted in Fig. 1(b) for $J_{\text{int}}/J_c = -0.5$. It can be deduced from the figures that boundaries of the dynamically ordered regions get narrower with a further increment in the external applied field amplitude. The physical mechanism underlying this observation is indicated above, therefore we will not discuss it here again. As a complementary investigation in the following analysis, let us center our interest upon the influences of the applied field period on the dynamic phase diagrams in $(J_{\text{int}}/J_c - T_c/J_c)$ planes and the thermal variations of core–shell magnetizations for selected Hamiltonian parameters in Fig. 4(a)–(b). It is possible to emphasize that the transition temperature of the particle gets lower with an increment of period. The physical explanation of this behavior is straightforward: At high oscillation period values, dynamic magnetization corresponding to the instantaneous ferrimagnetic order parameter of the particle can respond to the oscillating magnetic field with some delay, whereas when the period of the external magnetic field gets lower, a competition occurs between the period of the field and the relaxation time of the system, hence the dynamic magnetization cannot respond to the external field owing to increasing phase lag between the field and time dependent magnetization. As a result of this mechanism, the occurrence of the dynamic phase transition becomes difficult for the cubic
Fig. 5. (Color online) (a) Shell thickness dependencies of the dynamic critical point of a cubic nanoparticle system for selected Hamiltonian parameters such as $J_{\text{int}}/J_c = -1.0, J_{\text{sh}}/J_c = 0.5, \tau = 100$ with two applied field amplitudes $h = 0.0$ and 0.5. The influences of the shell thickness on the thermal variations of core–shell (b) and total (c) magnetizations of the particle for $J_{\text{int}}/J_c = -1.0, J_{\text{sh}}/J_c = 0.5, \tau = 100, h = 0.5$ and $d_{\text{shell}} = 3, 5, 7,$ and 9.

Fig. 6. (Color online) Influences of the varying (a) antiferromagnetic interface coupling parameter, (b) applied field amplitude and (c) shell thickness values on the thermal variations of heat capacities of a cubic nanoparticle system for some combinations of Hamiltonian parameters.

Core–shell nanoparticle under the influence of a driving time dependent magnetic field. The aforementioned situations can be seen clearly in Fig. 4(a)–(b).

To show the influences of the varying size of the particle on its thermal and magnetic properties, we give in Fig. 5(a) the dynamic phase boundaries in $(d_{\text{shell}} - T_c/J_c)$ plane for two selected applied field amplitudes $h = 0.0$ and 0.5 with $\tau = 100, J_{\text{int}}/J_c = -1.0$ and $J_{\text{sh}}/J_c = 0.5$. Here, $d_{\text{shell}}$ represents the shell thickness of the particle. One can readily observe that the dynamic phase transition point depends on the size of particle. Strictly speaking, the phase transition point increases with increasing $d_{\text{shell}}$ value starting from $d_{\text{shell}} = 2$. When the shell thickness of the particle reaches a certain value, the phase transition point saturates and does not significantly change. The saturation region of the particle strongly depends upon the Hamiltonian parameters. For example, the saturation line of the particle locates a relatively upper region in the related plane for $h = 0.0$ while with increasing applied field amplitude, say $h = 0.5$, it moves downward. On the other side, as seen in the Fig. 5(b) and (c), the varying shell thickness explicitly affects the thermal variations of core–shell and total magnetizations of the particle for selected values of Hamiltonian parameters such as $h = 0.5, \tau = 100, J_{\text{int}}/J_c = -1.0$ and $J_{\text{sh}}/J_c = 0.5$. This is an expected result since as the size of the particle increases the energy coming from the exchange coupling tends to increase, therefore, relatively more thermal energy needs to destruct the dynamically ordered region depending on other parameters.

As we mentioned before, the dynamic phase transition points have been calculated by making use of the thermal variation of heat capacity. From this point of view, as a final investigation, we give the temperature dependencies of heat capacities for some combinations of Hamiltonian parameters in Fig. 6(a)–(c) as well as varying shell thickness. For example, based
on the Fig. 6(a) corresponding to the dynamic phase diagram plotted in Fig. 1(a) with \( h = 0.25 \), it can be easily said that the dynamic heat capacity curves exhibit a sharp peak at the transition temperature, and when the absolute value of the \( J_{int}/J_c \) increases, the boundary of the dynamically ordered phase region gets wider, in other words, the location of the sharp peak shifts to a higher value in the temperature plane, namely, much more thermal energy needs to carry out a dynamic phase transition. According to our results, the heat capacity curves do not present the Schottky-like rounded hump at the relatively smaller value of \( J_{int}/J_c \), however, with an increment value of \( J_{int}/J_c \) it begins to show depending on the considered Hamiltonian parameters. Our calculations also indicate that the hump behavior located at the smaller temperature than the critical temperature is a result of a significant change in the core magnetizations. It is worthwhile to note that such kinds of treatments have been reported in some of the previously published works regarding the nonequilibrium dynamics of small sized particles [47,48]. In Fig. 6(b) we plot the external applied field amplitude dependencies of the heat capacity curves for values of \( \tau = 100, J_{int}/J_c = -1.0 \). In accordance with the expectations, increasing \( h \) value gives rise to a shift of the sharp peak location to inward in the reduced temperature plane. Furthermore, we see from the Fig. 6(c) that the critical temperature increases as the shell thickness of the particle increases, and the shape of the heat capacity curves are nearly same for selected \( d_{shell} \) values depending upon the other Hamiltonian parameters.

4. Conclusion

In this study, we have studied the stationary states properties of a ferrimagnetic core–shell nanocub system under the influence of a forcing oscillating magnetic field within the framework of MC simulation based on a standard Metropolis algorithm. The most conspicuous results underlined in the present work can be summarized as follows: (i) The global dynamic phase diagrams that separate the dynamically ordered and disordered phases strongly depend upon the amplitude and period of the applied magnetic field as well as other Hamiltonian parameters. For example, the phase transition temperature changes sharply for the high amplitude and period of the field at the relatively larger \( J_{int}/J_c \) value while the transition line exhibits smooth behavior for small \( J_{int}/J_c \) value in the related plane. (ii) Even though the core and shell exchange couplings of the nanoparticle are different from each other, due to the relatively strong antiferromagnetic interface coupling parameter, both core and shell sublattice magnetizations exhibit a second order phase transition at the same critical temperature. It is also beneficial to indicate that if the value of the \( J_{int}/J_c \) parameter is selected to be zero, the phase temperature points of core and shell layers will be different from each other due to different contributions coming from sublattices. In this situation, the same physical results may be obtained by keeping the particles side by side or nested. (iii) It is possible to point out that the dynamics of particle sensitively depends on the varying particle thickness. For instance, the critical temperature increases with the size of particle up to the thermodynamic limit of particle. (iv) The antiferromagnetic exchange coupling clearly affects the behavior and shape of the dynamic heat capacity. As we mentioned before, the strong antiferromagnetic interface coupling gives rise to the existence the local hump behavior located relatively low temperature in the thermal variation of heat capacity.

As a final comment, based on the previously published studies [47,48,51], it can be mentioned that hysteresis behaviors of the nanoparticle systems under a time dependent magnetic field explicitly depend on the selected Hamiltonian parameters. In our present study, this type of analysis is not studied due to the restricted computer facilities. Such a comprehensive work may be an interesting study, and unusual results may be obtained by looking at the hysteric properties of the considered system. Apart from these, it is possible to improve the proposed model to simulate more realistic systems by considering simulation of a Heisenberg type of Hamiltonian with an assembly of interacting nanoparticles instead of a single particle.

References