Thermal induced transition in 3D spin-crossover lattice with (anti)ferromagnetic surface under external fluctuations

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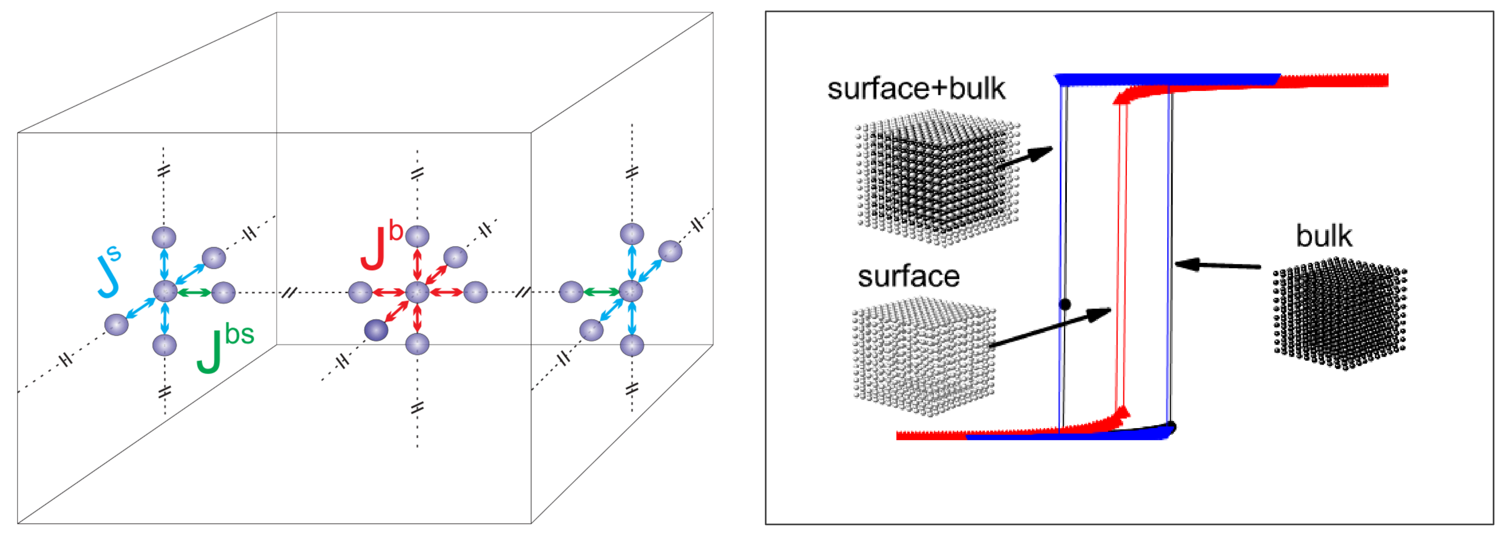
Abstract. The role of surface magnetization on thermal induced spin-crossover phenomenon for 3D cubic lattice in presence of correlated fluctuations has been studied. The ferromagnetic and antiferromagnetic ordering for the surface's sites was considered. By Monte Carlo simulation a thermal phase transition of spin-crossover nanocrystals with correlated and uncorrelated local random fields has been analyzed. It was shown the shifting of transition temperatures contributed by cooperativity of surface molecules in spin-crossover system under fluctuations. Also, we found that the nature of cooperativity for the sites on the surface has the drastic impact on the completeness of phase transition. The obtained results agree with experimental data.

Ising-like model of spin-crossover nanocrystal



(a) (b)

Fig. 1. The spatial configuration of a three-dimensional SCO system. The couplings of magnetic molecules situated on the surface and inside the lattice are illustratively shown in (a). In (b) is given the schematic representation of the division of entire system into subsystems (surface, bulk and interface layer).

The spin-crossover compounds are the transition coordination complexes with pseudo-octahedral symmetry containing metal ion surrounded by a ligand. The interactions in molecular spin-crossover nanoparticles can be modeled by the Ising-like Hamiltonian [1]. For studying the influence of surface's molecules, we split the interaction term into three separate couplings [2,3]. The Hamiltonian of the model is:

$$H = -J_s \sum_{<ij>} s_i s_j - J_{bs} \sum_{<ij>} s_i s_j - J_b \sum_{<ij>} s_i s_j - \sum_i h_i(t) s_i \quad (1)$$

where, $J_{s,bs,b}$ is short-range couplings between nearest neighbor sites: the one describing the coupling of molecules on the surface (J_s), the second one that is responsible for linking the bulk of nanocrystal with its surface (J_{bs}), and the last one describing the interaction of bulk molecules (J_b). Here, $h_i = \Delta - kT\ln g + \xi_i(t)$ is time dependent external field, where Δ is energy gap between HS and LS states, k is the Boltzmanns constant, g is the degeneracy ratio, $\xi_i(t)$ is the stochastic process describing the fluctuations in local random field (can be correlated and uncorrelated).

The manifestation of hysteresis in the system with (anti)ferromagnetic surface under fluctuations

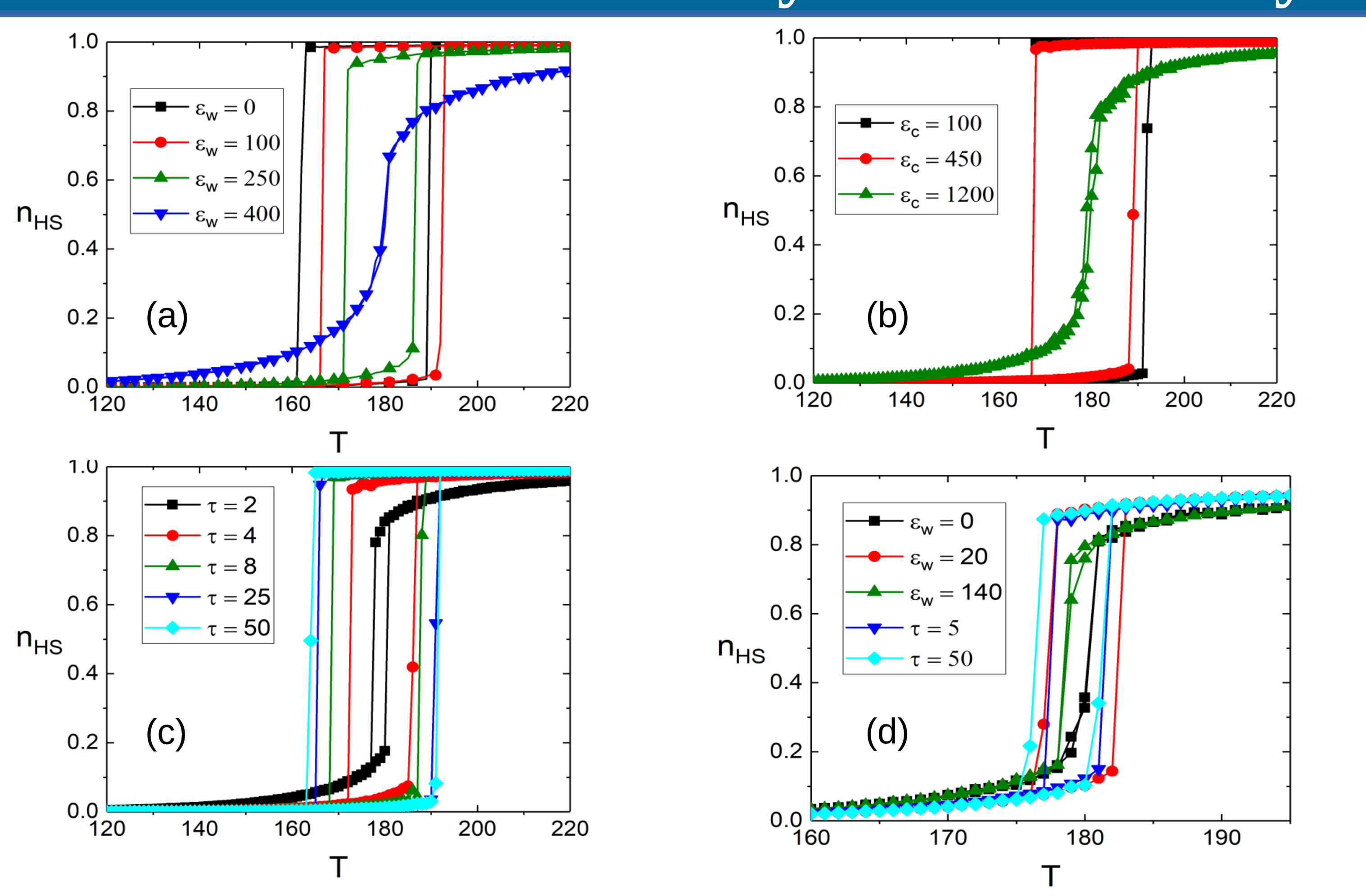


Fig. 2. The spin transition curves for different statistical characteristics of fluctuations for J = 85 in (a) providing the drastic transition and J = 55 in (d) for gradual transition (for τ = 5; τ = 10 the fluctuations is ε_c = 140). The hysteresis loops in (a) corresponds to fluctuationless system and to the system with uncorrelated fluctuations; in (b) the hysteresises are reproduced for the system with correlated in time (colored) fluctuations with autocorrelation time τ = 10; in (c) the impact of autocorrelation time of hysteretic behavior is analyzed for ε_c = 450. The system size is 10×10×10.

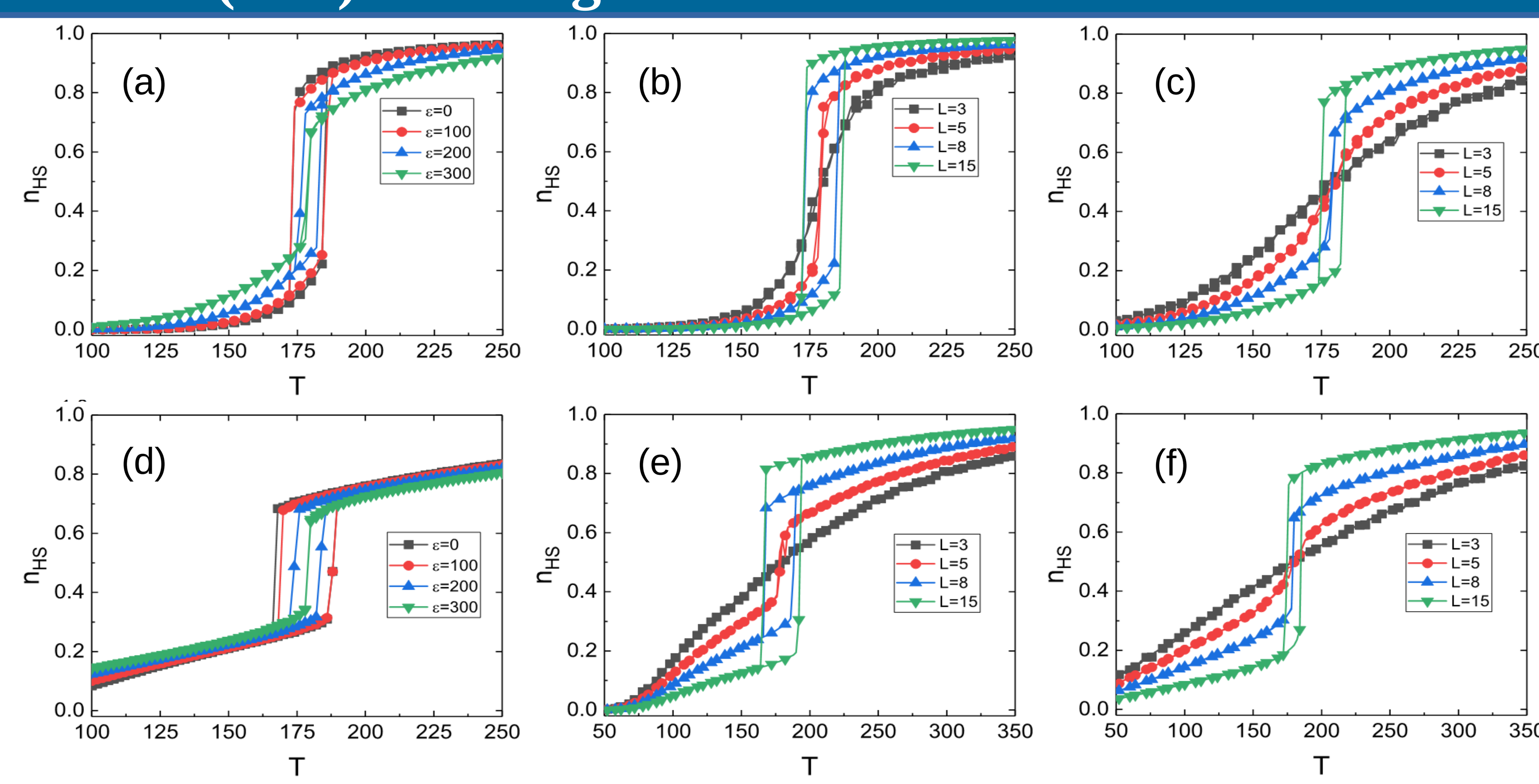
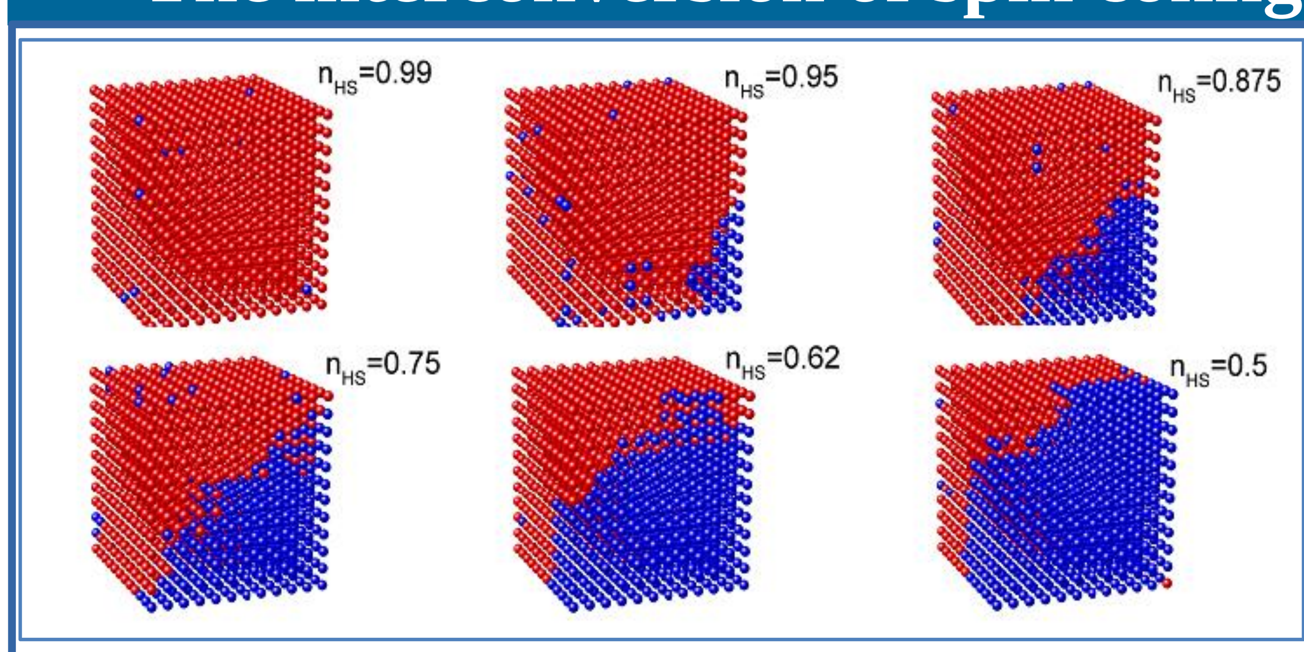
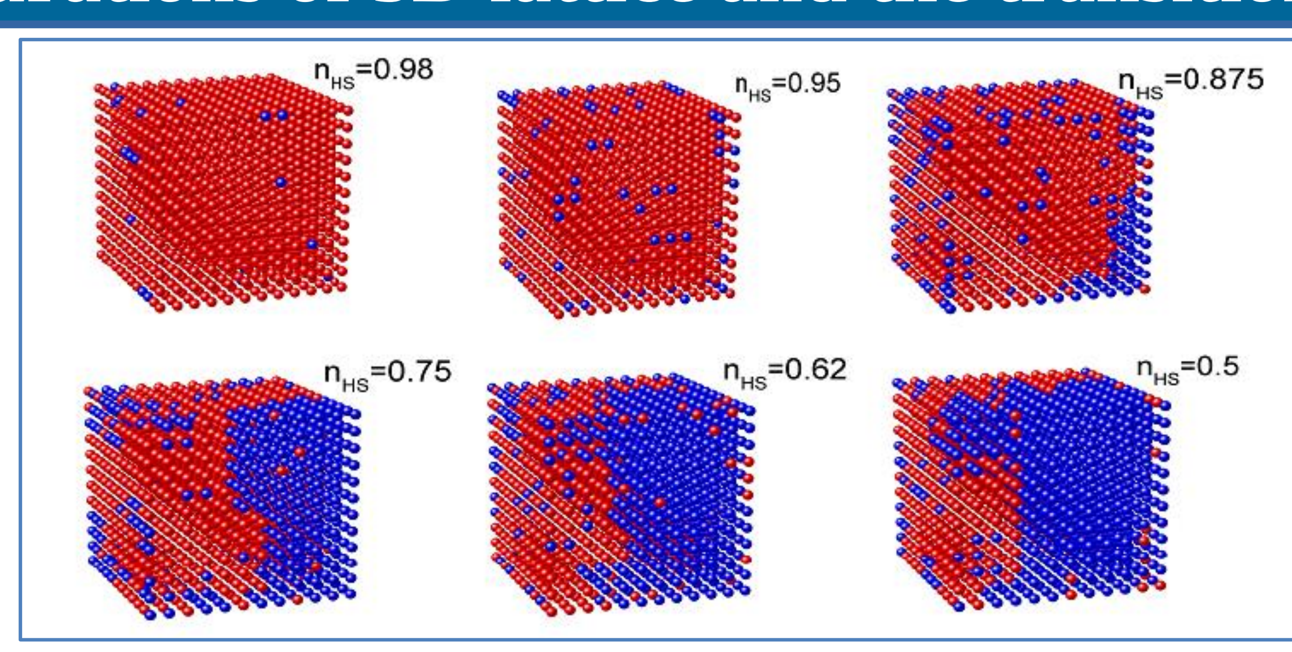


Fig. 3. The behavior of hysteresis loop for 3D spin-crossover system with different configuration of couplings for surface and for interface layer between surface and bulk part of nanocrystal: (a), (b), (c) are for $J_s = J_{bs} = 0.5J_b$; (d), (e), (f) are for $J_s = -0.5J_b$; $J_{bs} = 0.5J_b$. The panels (b) and (e) are for fluctuationless system whereas the plots from (c) and (f) are obtained for ε = 300 (only uncorrelated case is considered).

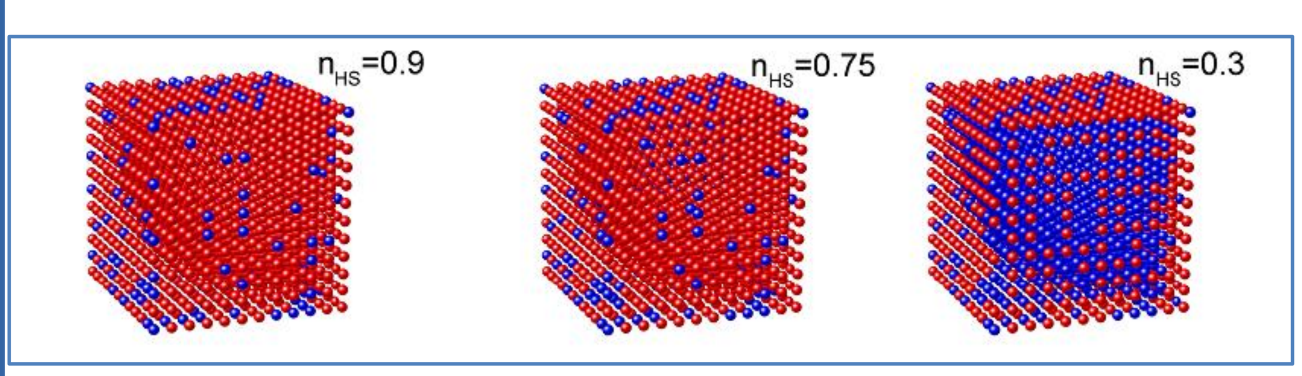
The interconversion of spin configurations of 3D lattice and the transition temperature of the system



(a)



(b)



(c)

Fig. 4. The spin configurations of the lattice at indicated values of high-spin fraction n_{HS} for fluctuationless case with surface coupling $J_s = J_b$ (a) and $J_s = 0.5J_b$ (b). The red circles indicate the molecules with HS configuration whereas the blue ones correspond to LS configuration. The spin configurations of the lattice for the value of surface coupling $J_s = 0.5J_b$ and fluctuations strength ε = 100 are given in (c). The weaker coupling of surface's molecules randomize their magnetization especially in the presence of fluctuations.

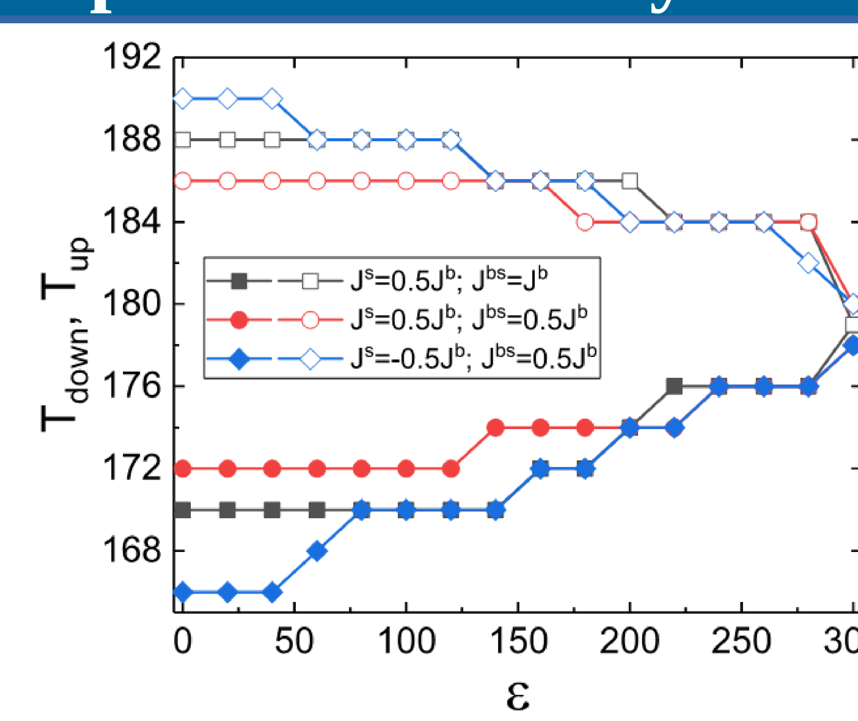


Fig. 5. The behavior of transition temperatures with increase of fluctuations strength. The data are obtained for 3D cubic lattice with side L = 8. Here, the filled markers are for temperatures of cooling branch and the empty ones are for transition temperatures during heating. The general tendency for all three configurations is the collapsing of hysteresis loop with increase of fluctuations strength.

Summary and conclusions

1. The spin-crossover magnetic nanoparticles that are depicted by Ising-like model with the accounting of correlated external random crystal field by means of Monte Carlo simulations are studied.
2. The strengthening of fluctuations of crystal field narrow the hysteresis width in case of first-order phase transition, however, the narrowing is dependent on the statistical characteristics of fluctuations (its strength and autocorrelation time).
3. For a system with antiferromagnetic coupling of surface's sites the temperature transition curves demonstrate a premature saturation with smaller magnetization value for HS state and greater one for LS configuration in contrast to the completely ferromagnetic system.

References

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