Spin-crossover behavior of iron molecular chain

Iu. Gudyma, yugudyma@gmail.com

Physical, Technical and Computer Sciences Institute of Yuriy Fedkovych Chernivtsi National University, Ukraine

INTRODUCTION The spin-crossover (SCO) compounds are the class of inorganic coordination molecular complexes of the chemical elements with d4-d7 electronic configurations of the outer orbital which form the ligand environment with transient metal ion centered in octahedral ligand field. These materials are characterized by two degenerate spin states: low-spin (LS) state with diamagnetic properties and high-spin (HS) state with paramagnetic behavior. The LS and HS spin configuration can be interchanged by the action of external controlling fields such as temperature, pressure, or light intensity.

Spin-crossover behavior appears as a result of the spin-elastic frustration. Depending on the particular configuration of the magnetic molecules, a variety of magnetization behaviors can be described even with a relatively simple model. Such studies could find a wide variety of practical applications, including further miniaturization of nanodevices and nanomaterials.

Quasi-one-dimensional systems play an essential role in nanotechnology. In this work, we consider a molecular chain of particles with two inner states. In our model, these two inner states may degenerate. The particles are subject to a pair potential of a general type, which differentiates the inner states of particles. We treat the model analytically using transfer-matrix formalism.

RESULTS In order to characterize the behavior of a 1D molecular chain considering both structural and magnetic properties, we are basing on the simple conception in which the molecules compound a coordination polymer.

We denote a higher energy state as a pseudo-spin +1 state and a lower energy state as a pseudo-spin -1 state. A spin +1 state has degeneracy g_+ and spin -1 has degeneracy g_-. We assume that pair interactions depend on the particle pseudo-states, and the potentials of the corresponding pairs of pseudo-spin state interactions are $V_{--}(r)$, $V_{+-}(r)$, and $V_{++}(r)$. A schematic view of the three microscopic configurations of two neighboring atoms in the chain is shown in Fig. 1(a). The Hamiltonian of the system is a sum of the pair potentials and a single-particle field,

$$\hat{H} = \sum_{n=1}^{N-1} V_{s_n s_{n+1}}(x_n - x_{n+1}) + \sum_{n=1}^{N} W_{s_n},$$

where N is the total number of molecules and W_{s_n} is the energy of the single-molecule pseudo-state. The difference of the pseudo-state energies $\Delta = W_+ - W_-$ is the external ligand field acting on a single molecule. We apply a harmonic approximation for the pair nearest-neighbor potential $V_{s_n s_{n+1}}(r)$ at the potential minimum,

$$V_{s_n s_{n+1}}(r) = V_{s_n s_{n+1}}^{(0)} + \frac{1}{2} K_{s_n s_{n+1}} \left(r - a_{s_n s_{n+1}} \right)^2,$$

Where $a_{s_n s_{n+1}}$ is a distance where potential has minimum, $V_{s_n s_{n+1}}^{(0)}$ is the potential depth, and $K_{s_n s_{n+1}}$ is an elastic constant coupling nth and (n+1)th molecules in the pseudo-states s_n and s_{n+1}. Schematic treatment of the potentials is shown in Fig. 1(b).
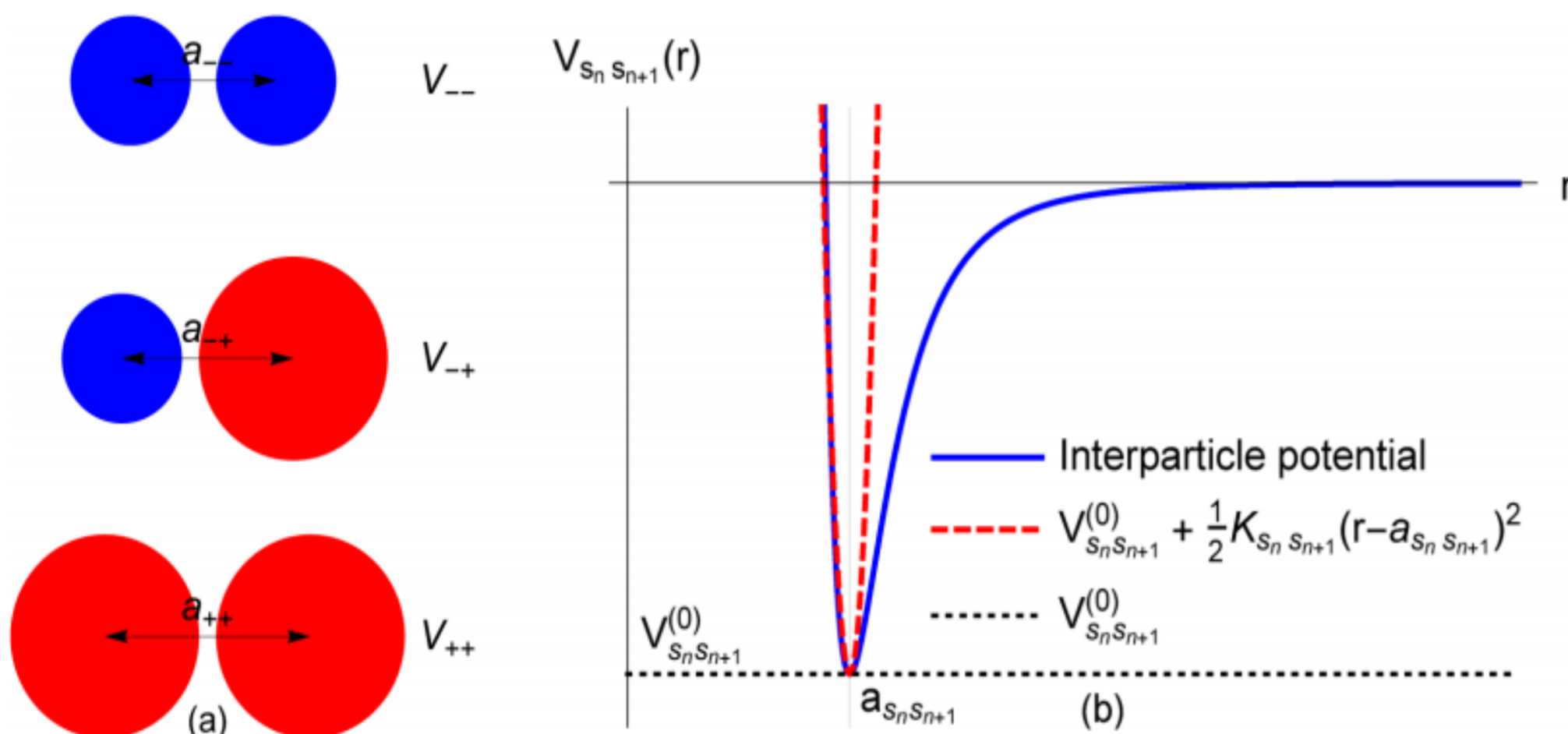
Fig. 1. Schematic interactions of the pseudo-spin states and treatment of the inter-particle potential. (a) All possible configurations of the nearest pseudo-spin states. Interaction potentials and average distances between particles depend on the pseudo-spin states. (b) Interaction potential and harmonic approximation. We consider possible displacement of the particles from the equilibrium position for the given pseudo-state configuration to be small.

The statistical properties of the model are completely determined by the partition function

$$Z = \sum_{\{s_1,\dots,s_N\}} \iiint dq_1 \cdots dq_{N-1} g_{s_1} \cdots g_{s_N} e^{-\beta E(q_1,\dots,q_{N-1},s_1,\dots,s_N)}$$

$$= \sum_{\{s_1,\dots,s_N\}} g_{s_1} \cdots g_{s_N} \left(\prod_{n=1}^{N-1} \sqrt{\frac{2\pi}{\beta K_{s_n s_{n+1}}}} \right) e^{-\beta E_1},$$

where the sum is over all states $\{s_1, \dots, s_N\}$ with energy $E(s_1, \dots, s_N)$, g_{s_n} represents the degeneracy of the state s_n, and β denotes the inverse of the Boltzmann constant times temperature. It is convenient to consider an ensemble in which Z depends on the temperature and the field. Certainly, the choice of boundary conditions becomes irrelevant in the thermodynamic limit.

The partition function can be expressed as the partition function of the Ising model with the effective Hamiltonian

$$\hat{H}_{eff} = E_{0,eff} - \sum_{n=1}^{N-1} J_{eff} \hat{s}_n \hat{s}_{n+1} - \sum_{n=2}^{N-1} B_{eff} \hat{s}_n + \frac{B_{boundary} + B_{eff}}{2} (\hat{s}_1 + \hat{s}_N),$$
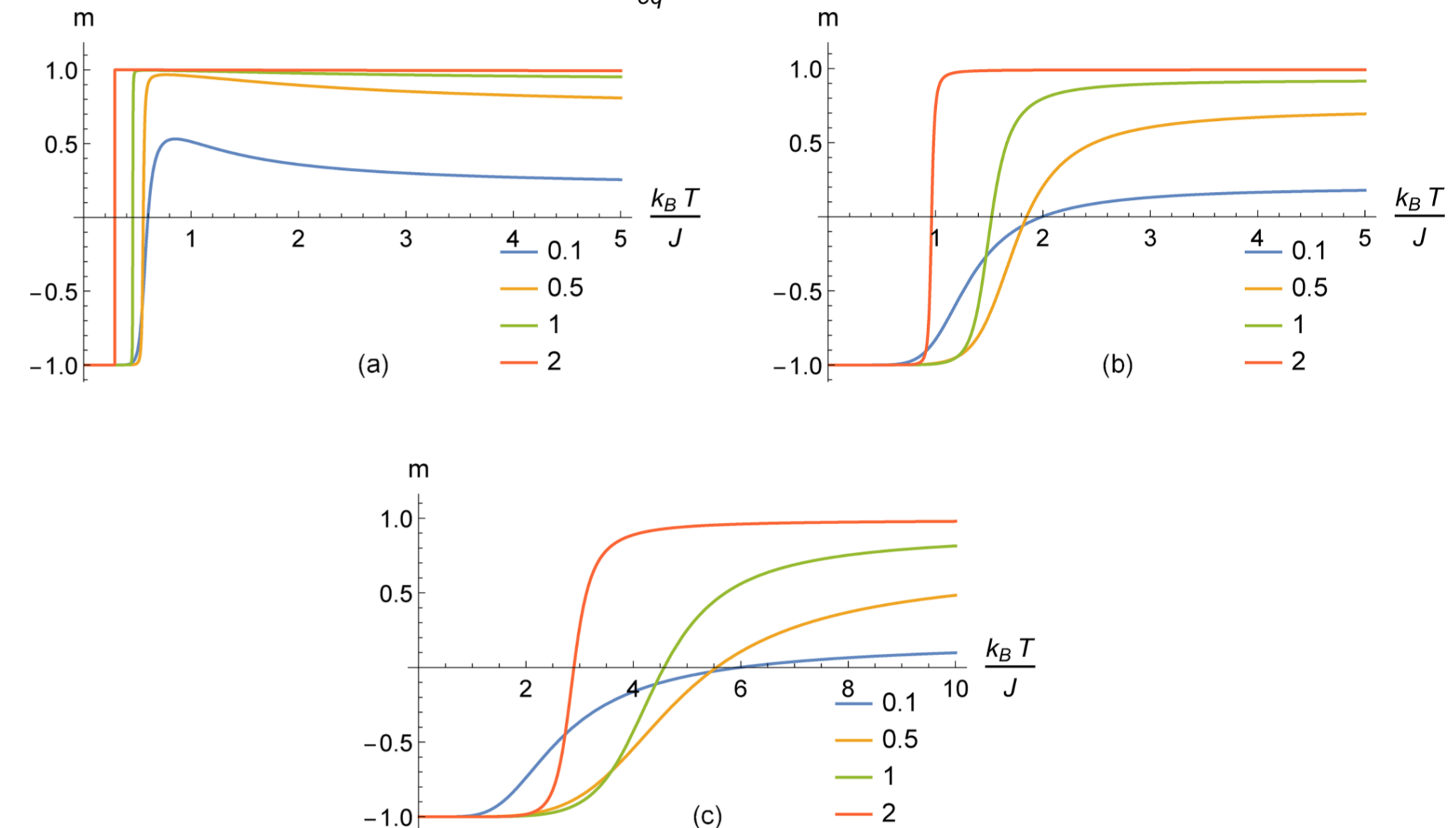
where $E_{0,eff} = E_0 - \frac{N k_B T}{2} \ln g_+ g_- - (N-1)\delta \epsilon k_B T$, $J_{eff} = J + \delta j k_B T$, $B_{eff} = B + \frac{k_B T}{2} \ln g + \delta b k_B T$, and $B_{boundary} = -\frac{\Delta}{2} + \frac{k_B T}{2} \ln g$.

The effective Hamiltonian coincides with the Ising model Hamiltonian with the reference energy, effective magnetic field, and ferromagnetic interaction constant being functions of temperature. This dependence roots from taking into account pseudo-states degeneracy and phononic interactions.
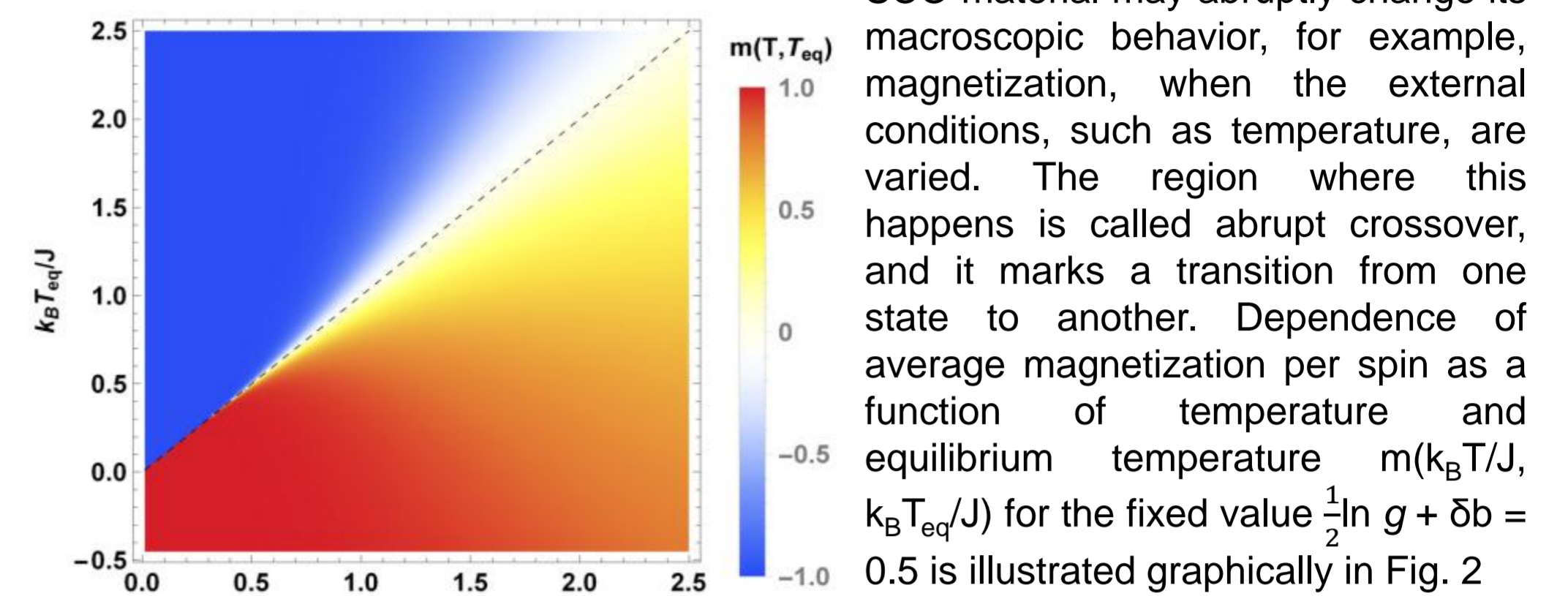

Fig. 2. Average magnetization $m(T, T_{eq})$ for $\frac{1}{2}\ln g + \delta b = -0.5$ and $\delta j = 0$. The dashed line indicates condition $T = T_{eq}$.

SCO material may abruptly change its macroscopic behavior, for example, magnetization, when the external conditions, such as temperature, are varied. The region where this happens is called abrupt crossover, and it marks a transition from one state to another. Dependence of average magnetization per spin as a function of temperature and equilibrium temperature $m(k_B T/J, k_B T_{eq}/J)$ for the fixed value $\frac{1}{2}\ln g + \delta b = 0.5$ is illustrated graphically in Fig. 2

FIG. 3. (a)–(c) Average magnetization as a function of temperature for $T_{eq} < T_{crossover}$, $T_{eq} = T_{crossover}$, and $T_{eq} > T_{crossover}$ and various values of the $\frac{1}{2}\ln g + \delta b = 0.1, 0.5, 1, 2$ and $\delta j = 0.35$. In the case $T_{eq} < T_{crossover}$, average magnetization has maximum at $T = T_0$. For $T_{eq} = T_{crossover}$, maximum is reached at $T_0 = \infty$. When $T_{eq} > T_{crossover}$, average magnetization is a monotonous function of temperature and has no extrema.
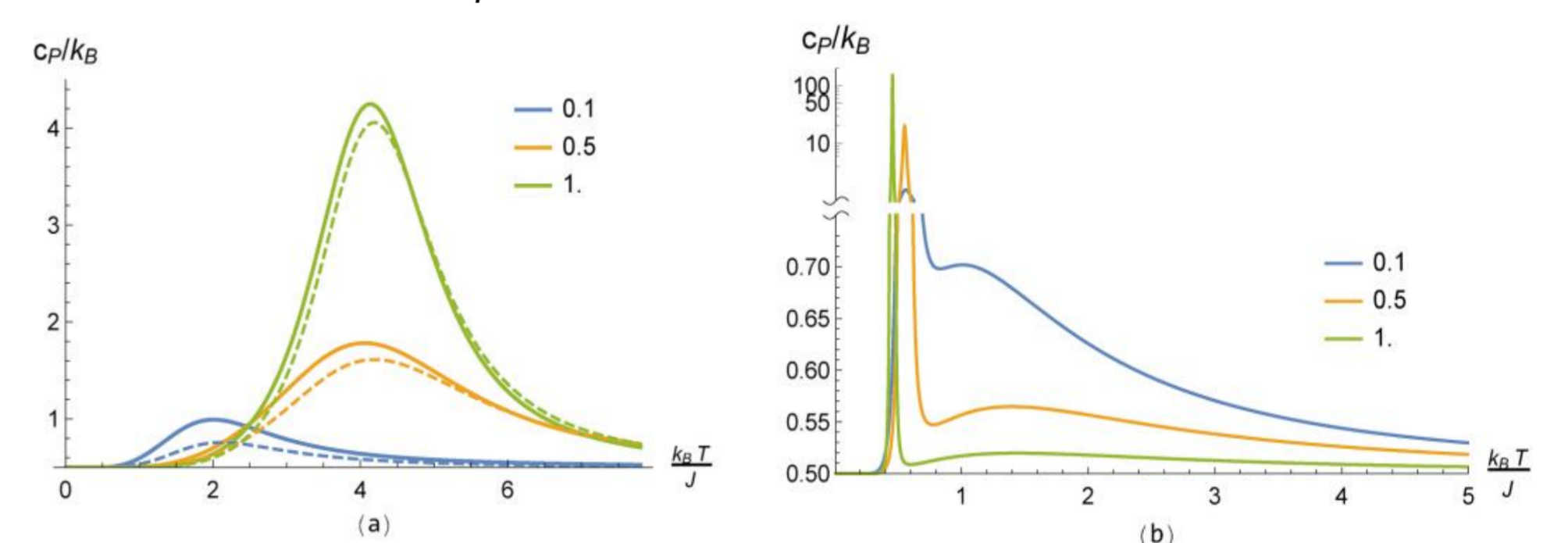
FIG. 4. Specific heat capacity per particle c_P (solid line) as a function of temperature and the $-B\frac{\partial m}{\partial T}$ derivative (dashed line). (a) $T_{eq} = 3T_{crossover}$. Parameters are chosen to be same as Fig. 3(c). Maximum of the heat capacity is shifted from the maximum of the derivative $\frac{\partial m}{\partial T}$. (b) $T_{eq} = 0.3T_{crossover}$. Parameters are chosen to be same as in Fig. 3(a).

CONCLUSION

❖ We have systematically studied the one-dimensional molecular chain with degenerate states and phononic interaction. Exact solutions by the method of transfer matrix modified for free boundary were obtained.

❖ We have shown that there is an exact mapping between the elastic molecular chain and Ising models of SCO materials.

❖ We have analyzed the regimes of the LS–HS crossover and identified if the crossover is abrupt or gradual for the specific parameters. In the case of abrupt crossover we have showed possibility of existing two peak thermal dependence of the specific heat capacity.

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