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Short-time Monte Carlo study on the phase transition of a ferromagnetic polymer chain model

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Abstract

Short-time dynamic scaling analysis method is applied to investigate the phase transition of a ferromagnetic Ising chain model on the simple cubic lattice. The phase transition temperature T_c is determined from the time evolutions of magnetization $M(t)$ and square magnetization $M^2(t)$ at temperatures near T_c. The resulted T_c is consistent with that obtained from the annealing Monte Carlo method. The short-time dynamic behaviors of magnetizations near the transition temperature are also studied. We find both $M(t)$ and $M^2(t)$ show power law decay near T_c after a very short time period $\tau_{\text{mic}} \approx 100$ Monte Carlo steps.

Keywords: Phase transition; Magnetic polymers; Scaling

1. Introduction

Short-time Monte Carlo (MC) method has witnessed great success since Janssen et al. discovered that a universal dynamic scaling form exists in the macroscopic short-time regime [1]. A number of MC simulations confirmed the existence of such a short-time dynamic behavior [2–8]. When a system initially at high temperature disordered state or at zero temperature ground state (GS) is quenched to the critical temperature, a universal short-time behavior emerges after a microscopic time scale τ_{mic} [3,8]. The short-time dynamic scaling form provides a new technique for measuring the critical temperature as well as both dynamic and static critical exponents [3,5,8]. It had been used to determine the second-order phase transition temperature of many magnetic systems, such as two-dimensional (2D) and three-dimensional (3D) Ising models, XY model, etc. [3,8–11].

In this work, we apply the short-time dynamic scaling to determine the phase transition of a ferromagnetic Ising polymer chain model. The Ising polymer chain model is a reasonable model that can describe some physical aspects of magnetic polymers in dilute solutions. Theoretical design of magnetic polymer is based on the magnetic interactions among spins and a lot of experimental results can be well explained by Ising or Heisenberg interactions among spins [12–16]. It was expected that the flexibility, low loss, thin-film-forming ability, and low density will ensure the ferromagnetic polymers play important roles in technology [17], such as in fields of communication, energy and information. The Ising polymer chain model adopted in this paper is a coarse-grained bond fluctuation model [18] on the simple cubic (SC) lattice with spatial nearest neighbor (NN) ferromagnetic Ising interaction [19]. The model chain undergoes a magnetic phase transition as well as a spatial configurational collapse transition at the critical temperature T_c at zero field [20]. It was also found that both magnetic and spatial configurational properties are dependent on external fields: different field dependent behaviors are observed at temperatures below and above the critical temperature T_c [21].

2. Model and simulation method

The 3D Ising chain model on the SC lattice is described by the following Hamiltonian:

$$H = -\sum_{[ij]} J_{ij}\sigma_i\sigma_j \tag{1}$$

where $\sigma_i = \pm 1$ are the spin variables at monomers of the chain. The features of the model are reflected in the spin–spin couplings J_{ij}. In this work, we consider spatial NN interactions

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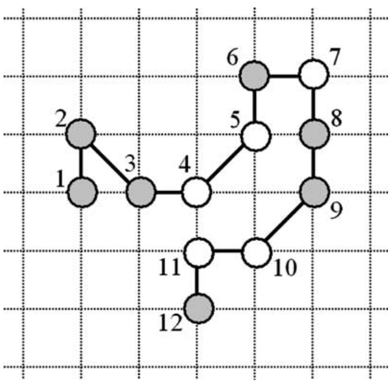

Sketch 1. One configuration of an Ising chain on the square lattice. Circles represent monomers of the chain. Grey circle and empty circle represent spin up ($\sigma=1$) and spin down ($\sigma=-1$), respectively. Nearest neighbor number depends on spatial configuration. For example, monomer 4 has two nearest neighbors 3 and 11, while monomer 8 has three nearest neighbors 5, 7 and 9.

with $J_{ij}=J$ for $[ij]$ nearest neighbor on the lattice and zero otherwise, i.e. the spin–spin interactions exist only between a pair of spins with spatial distance $r_{ij}=|\vec{r}_i-\vec{r}_j|$ one lattice apart, see Sketch 1. Here we consider the ferromagnetic case and set the coupling constant $J=1$ for simplification. The excluded volume of the monomer is also taken into account by the self-avoiding requirement that no lattice site can be occupied simultaneously by two or more monomers. The spin variable in this model has two values $\sigma_i=\pm 1$, corresponding to the spin quantum number $S=1/2$.

The polymer chain of chain length n is comprised of n identical monomers (monomer numbered from 1 to n) consecutively linked with a variable bond length on the SC lattice. Each monomer occupies one site of the lattice. The chain's bond length can fluctuate among values 1, $\sqrt{2}$ and $\sqrt{3}$ in the unit of the lattice constant which is set as unit of length [22]. The bond between successive monomers can be taken from a set of 26 allowed bond vectors obtained from the set {(1,0,0), (1,1,0), (1,1,1)} by symmetry operations of the cubic lattice.

A chain configuration comprises spatial and spin configurations. The former describes the spatial arrangement of monomers and the latter describes the arrangement of spins. Therefore, the dynamics of the chain's configuration contains two aspects: updating spatial configuration and updating spin configuration. The evolution of the spatial configuration starts by randomly choosing a monomer and then attempts to move it one lattice spacing in a direction randomly selected from six possibilities: $\pm x$, $\pm y$, $\pm z$. This trial move will be accepted if all the following four conditions are satisfied: (1) self-avoidance is obeyed, (2) the new bond vector still belongs to the allowed bond set, (3) two bonds do not intersect, and (4) the Boltzmann factor $\exp(-\Delta E/k_{\mathrm{B}}T)$ is greater than a random number uniformly distributed in the interval (0, 1), where ΔE is the change in energy due to the trial move. The fourth criterion, i.e. the Metropolis criterion, ensures that the system obeys Boltzmann statistics at a specific temperature [23,24]. To update the spin configuration, we randomly choose a monomer and flip the spin on it according to the Metropolis criterion. The time unit used in the work is MC step (MCS). One MCS includes n monomer trial movements and n trial spin flips.

Our dynamic MC simulation is consisted of two main steps. First, we anneal the system to obtain a GS at approximate zero temperature, then we perform short time dynamics near T_{c} after quenching the annealed GS to a temperature near T_{c}. The details of our simulation are described below.

Simulation starts from an initial random configuration at temperature much higher than the phase transition temperature. Then we slowly decrease the temperature with a variable temperature step ΔT. A small ΔT is used near T_{c} since physical properties vary faster near T_{c} while a large ΔT is used at temperatures far away from T_{c} since physical properties change little at high or low temperatures. At each temperature, system is updated for total $500n^2$ MCS and thus 500 samples are recorded with a time interval $\Delta t=n^2$ MCS. The final configuration at the previous temperature is used as the initial configuration for the subsequent temperature. The final configuration at $T=0.1$ is considered as the annealed GS since the configuration roughly does not change after T is less than 0.5. We totally generated 25 GSs, therefore we have 12,500 samples in the calculation of configurational properties. The short-time dynamics of the Ising chain is studied by quenching the GS to a temperature near T_{c}. We have simulated 500 different evolutions by using different random seeds for each GS thus we have also 12,500 samples for average. The reason we use different random seeds instead of generating a large number of GSs is that we find all annealed ground states are similar: a roughly compacted sphere with all spins align in the same direction. In the work, the temperature T is in the unit J/k_{B}, the energy is in unit of J. The chain length we used is $n=300$. Though the phase transition temperature depends on the chain length n, we find that chain length $n=300$ is long enough for studying magnetic and configurational properties [20].

3. Results and discussions

The spatial autocorrelation function (ACF) [25]

$$C_{\mathrm{RG}}(t)=\frac{\langle (R_{\mathrm{g}}(t)-\langle R_{\mathrm{g}}\rangle)(R_{\mathrm{g}}(0)-\langle R_{\mathrm{g}}\rangle)\rangle}{\langle R_{\mathrm{g}}^2\rangle-\langle R_{\mathrm{g}}\rangle^2} \tag{2}$$

and the magnetic ACF

$$C_{\mathrm{M}}(t)=\frac{1}{n}\sum_{i=1}^{n}\langle \sigma_i(0)\sigma_i(t)\rangle \tag{3}$$

are measured for the Ising chain model. Here the brackets $\langle\,\rangle$ denote ensemble average approximated over time and samples. R_{g} is the radius of gyration. The results of both ACFs are presented in Fig. 1. We find the drop of C_{RG} is very slow comparing with that of C_{M}, i.e. the relaxation of spatial configuration is much longer than the relaxation of spin

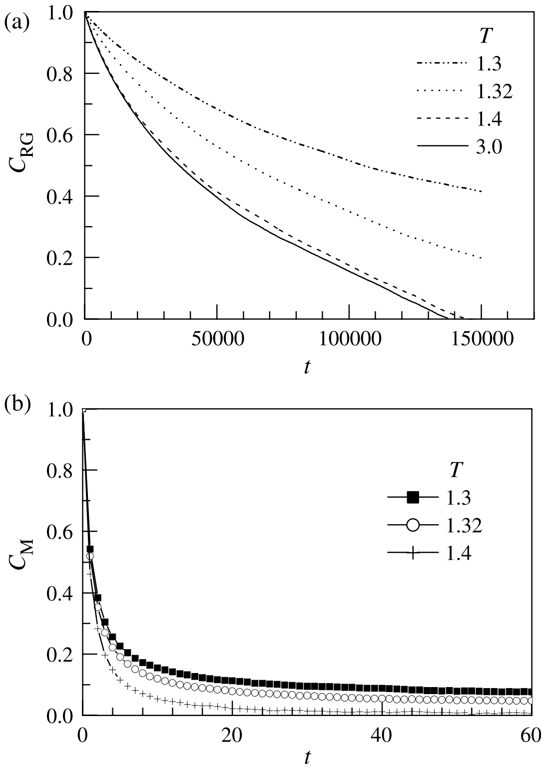

Fig. 1. Plots of (a) the spatial autocorrelation function C_{RG} and (b) magnetic autocorrelation function C_M as a function of time t for chain of length $n=300$ at several temperatures.

configuration. The relaxation time can be calculated as [25]

$$\tau_r = \int_0^\infty C(t)\mathrm{d}t \tag{4}$$

We find the relaxation time of spatial configuration τ_r is about 50,000 MCS at $T=1.4$, which is smaller than the sampling time interval $\Delta t = n^2 = 90{,}000$ MCS for $n=300$. That ensures us to obtain independent samples at high temperatures. However, the relaxation time τ_r increases with the drop of temperature when $T<T_c$. And at temperatures far below T_c, the configuration almost does not change and τ_r approach infinite. Therefore, we use conventional annealing method with fixed time interval in sampling below T_c [20,26,27].

It is well known that cluster algorithms, such as the Swendsen-Wang and the Wolff algorithms [28,29], can decrease relaxation time of spin system by introducing global updating of spin clusters. However, Fig. 1 shows that the relaxation of spatial configuration is several orders slower than that of spin configuration. That is, updating spatial configuration is a more time-consuming process. Therefore, we did not use cluster algorithms to update spins.

The order parameter for studying the phase transition is the magnetization which is defined as the average spin moment per monomer,

$$M = \frac{1}{n}\sum_{i=1}^{n}\sigma_i \tag{5}$$

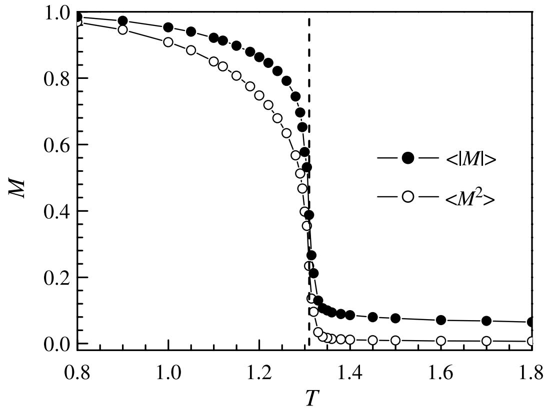

Fig. 2. Dependence of absolute and square magnetizations $\langle|M|\rangle$ and $\langle M^2\rangle$ on the temperature T for chain of length $n=300$. Vertical straight dash line at $T=1.31$ indicates the temperature at which both $\langle|M|\rangle$ and $\langle M^2\rangle$ vary fastest.

The magnetization M varies from 0 for a disordered state to 1 for an ordered state. At first we present the results obtained from the annealing MC simulations where the system is cooled from $T=4.0$ to 0.1. Since the statistical averaged magnetization $\langle M\rangle$ equals zero at zero field, we therefore, use mean absolute magnetization $\langle|M|\rangle$ and mean square magnetization $\langle M^2\rangle$ instead. Fig. 2 shows the dependence of $\langle|M|\rangle$ and $\langle M^2\rangle$ on the temperature T for the chain of length $n=300$. Both $\langle|M|\rangle$ and $\langle M^2\rangle$ varies from nearly zero at high temperatures to roughly 1 at low temperatures, indicating that the model has spontaneous magnetization at low temperatures. This reveals that the 3D Ising chain model differs from 1D Ising chain model; the latter has no spontaneous magnetization at all. We find the critical temperature $T_c \approx 1.31$ at which both $\langle|M|\rangle$ and $\langle M^2\rangle$ change fastest, or the absolute values of the differentiations $\mathrm{d}\langle|M|\rangle/\mathrm{d}T$ and $\mathrm{d}\langle M^2\rangle/\mathrm{d}T$ reach maximum.

Fig. 3 gives some typical configurations at different temperatures. At temperatures higher than T_c, the chain is in an extended coil state as shown in Fig. 3(a). And the summation of spins $\sum_{i=1}^{n}\sigma_i$ roughly equals zero. It is clear to observe many small spin clusters at temperatures above T_c.

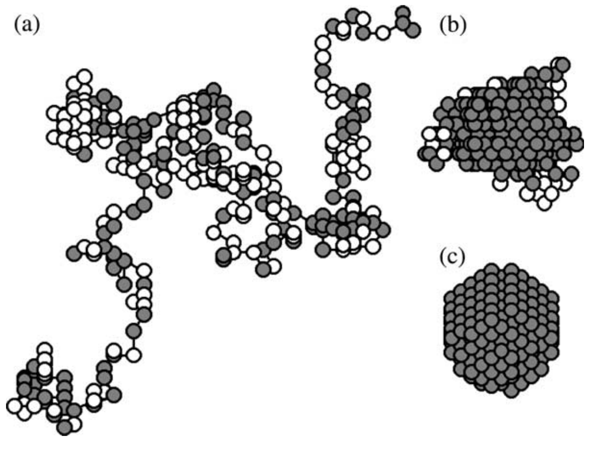

Fig. 3. Typical chain configurations at different temperatures T: (a) $T=1.6$ ($>T_c$); (b) $T=1.0$ ($<T_c$); (c) $T=0.01$. Chain length is $n=300$, and the phase transition temperature T_c is about 1.31. Grey and white circles are spins with $\sigma=1$ and $\sigma=-1$, respectively.

This observation confirms our previous analysis on the dependence of configurational energy of Ising chain on the temperature [20], where we found that the chain energy steadily decreases while the magnetization maintains roughly zero at $T > T_c$. At low temperatures $T < T_c$, a sphere like chain configuration forms and almost all spins align in the same direction, as shown in Fig. 3(b) and (c). Below T_c, configuration changes little with the decrease of temperature. An ordered configuration forms at very low temperature as shown in Fig. 3(c). For the current chain model, it is clear to observe the cooperation of spin and spatial configurations that was proved very important in the phase transition of the Ising chain model [20].

Starting from the annealed GS, we quench the system to a temperature near T_c. As we know, configuration changes a little in the short-time region so we set $M = 1$ for all the GSs by flipping all spins of those states with $M = -1$. Thus the mean magnetization M will always be positive in the short-time region. Based on the short-time dynamic scaling theory, the scaling form of kth order moment of the magnetization for the dynamic relaxation of a magnetic system, quenched from an initial ordered state, is given by [8]

$$M^k(t,\tau,L) = b^{-k\beta/\nu} M^k(b^{-z}t, b^{1/\nu}\tau, b^{-1}L) \tag{6}$$

where $\tau = (T - T_c)/T_c$ is the reduced temperature, t is the time, b is a scaling factor. And L is the size of simulated system. This scaling form is assumed to hold in the macroscopic short-time regime after a microscopic time scale τ_{mic} [8]. Usually, short-time simulations are carried out for a square or cubic system with system size L in all dimensions, e.g. 2D or 3D Ising systems. In these systems, order parameter is dependent on the system size L. However, the natural size of chain system in dilute solution will be the chain length n. To simulate polymer in dilute solution, we use a large cubic box to ensure box size $L \gg \sqrt{\langle R_g^2 \rangle}$ or $L \gg n^{0.6}$ for a SAW chain, thus the effect of the box on the chain can be ignored. Here, $\langle R_g^2 \rangle$ is the mean square radius of gyration. In this work, a box of size $L = 120$ is used. For this case, the properties of chain model do not depend on the size of simulation box but only depend on the chain length. Therefore, we expand the short-time scaling form (6) by replacing the system size L by the chain length n and get

$$M^k(t,\tau,n) = b^{-k\beta/\nu} M^k(b^{-z}t, b^{1/\nu}\tau, b^{-1}n) \tag{7}$$

for chain models.

For a sufficiently long chain, we can deduce the scaling behavior for the magnetizations M and M^2 ($k = 1$ and $k = 2$ in Eq. (7)), respectively. By setting the scaling factor b in the scaling form (7) as $b = t^{1/z}$, we get

$$M(t,\tau) = t^{-\beta/\nu z} G_1(t^{1/\nu z}\tau) \tag{8}$$

for $k = 1$ and

$$M^2(t,\tau) = t^{-2\beta/\nu z} G_2(t^{1/\nu z}\tau) \tag{9}$$

for $k = 2$. At the critical temperature T_c, $\tau = 0$, the magnetizations are expected to have the best power law behaviors since now $G_1(0)$ and $G_2(0)$ are independent of time t. Therefore, we can deduce the critical temperature T_c from the time evolution of magnetization M and square magnetization M^2. In this work, we have calculated the mean values $\langle M \rangle$ and $\langle M^2 \rangle$ from 12,500 samples.

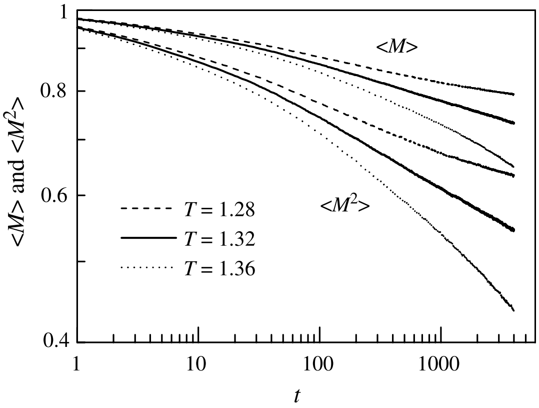

Fig. 4. Log–log plot of the evolution of mean magnetization $\langle M \rangle$ and mean square magnetization $\langle M^2 \rangle$ with time t at temperatures $T = 1.28$, 1.32, and 1.36, respectively.

Fig. 4 gives the log–log evolution of the mean magnetization $\langle M \rangle$ and mean square magnetization $\langle M^2 \rangle$ at temperatures $T = 1.28$, 1.32 and 1.36. At the very beginning, all curves have the same behavior: they decrease with time. Different behavior emerges after a microscopic time scale $\tau_{\mathrm{mic}} = 100$: log–log $\langle M \rangle - t$ (or $\langle M^2 \rangle - t$) curves are concave at low temperatures while they are convex at high temperatures. Therefore, a straight line with power law decay at T_c is expected as Eqs. (8) and (9). It is clear that the transition temperature is between 1.28 and 1.36.

In order to precisely locate the critical temperature T_c, we have also calculated the mean magnetization $\langle M \rangle$ and square magnetization $\langle M^2 \rangle$ at temperatures $T = 1.30$ and 1.34. For instance, Fig. 5 presents the evolution of mean square magnetization $\langle M^2 \rangle$ with time t after a microscopic time scale $\tau_{\mathrm{mic}} = 100$. With the magnetizations obtained at these five temperatures, we calculate the values of magnetization at other

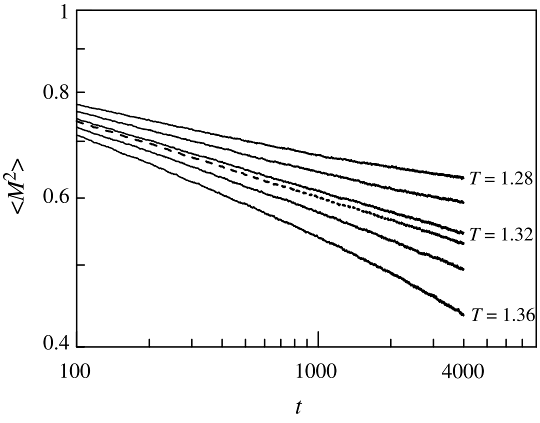

Fig. 5. Log–log plot of the evolution of mean square magnetization $\langle M^2 \rangle$ with time t after a microscopic time scale $\tau_{\mathrm{mic}} = 100$. Solid curves are Monte Carlo results at temperatures $T = 1.28$, 1.30, 1.32, 1.34 and 1.36 (from the top to bottom), respectively. Dash line is the best linear fitting with the critical temperature $T_c = 1.324$.

temperatures within (1.30, 1.34) with a temperature step 0.001 by using quadratic interpolation method. At every temperature, the deviation of the magnetization from the power law is calculated as the square deviations: $\mathrm{SD} = \sum_t [\langle M^2\rangle(t) - y(t)]^2$ in the time interval (100, 4000), here the power function $y(t) = C_1 t^{-C_2}$ is obtained by linear fitting of log–log $\langle M^2\rangle - t$ curve in Fig. 5. The temperature at which the square deviation is minimum is defined as the critical temperature T_c. With this method, we have determined the transition temperature T_c and the decay rate of the magnetizations at T_c. We find the magnetization $\langle M\rangle$ and the square magnetization $\langle M^2\rangle$ give roughly the same results: $T_c = 1.318$ and $\beta/\nu z = 0.044$ from $\langle M\rangle$ and $T_c = 1.324$ and $\beta/\nu z = 0.043$ from $\langle M^2\rangle$. The phase transition temperature obtained from the short-time scaling analysis is very close to that determined from the annealing method where $T_c = 1.31$ is found. We, therefore, conclude that the short-time dynamic Monte Carlo method can be used to determine the phase transition temperature of Ising polymer chain model.

From Figs. 4 and 5, one can see that both $\langle M\rangle$ and $\langle M^2\rangle$ do not reach their equilibrium values: finite values below T_c and roughly 0 above T_c. That means in the short-time regime the system is not in the equilibrium state. In other words, our short-time dynamic simulations are performed in states far away from the equilibrium states at or near T_c. Therefore, the short-time MC simulations do not suffer from the critical slowing down which makes the MC sampling very inefficient near T_c. The short-time dynamic scaling method provides a new method to locate the phase transition temperature of magnetic chain models.

4. Conclusion

We applied short-time dynamic scaling analysis method to determine the phase transition temperature T_c of a ferromagnetic Ising chain model on the simple cubic lattice. The initial ground states with magnetizations $M = M^2 = 1$ are firstly generated by annealing the system from high temperature to low temperature. We then quench the system to temperatures near the phase transition temperature T_c and simulate the evolution of magnetization $\langle M\rangle$ and square magnetization $\langle M^2\rangle$ at these temperatures. We determine $T_c = 1.318$ from $\langle M\rangle$ and $T_c = 1.324$ from $\langle M^2\rangle$ using short-time scaling analysis method. The resulted T_cs are in agreement with that obtained from the annealing Monte Carlo method. After a very short-time period $\tau_{\mathrm{mic}} \approx 100$ Monte Carlo step, both $\langle M\rangle$ and $\langle M^2\rangle$ show power law decay near T_c with critical exponent $\beta/\nu z \approx 0.044$.

Acknowledgements

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References

[1] Janssen HK, Schaub B, Schmittmann B. Z Phys B 1989;73:539.
[2] Huse DA. Phys Rev B 1989;40:304.
[3] Zheng B. Int J Mod Phys B 1998;12:1419.
[4] Luo HJ, Schulz M, Schülke L, Trimper S, Zheng B. Phys Lett A 1998; 250:383.
[5] Li ZB, Schülke L, Zheng B. Phys Rev E 1996;53:2940.
[6] Luo HJ, Schülke L, Zheng B. Phys Rev E 1998;57:1327.
[7] Jaster A. Phys Lett A 1999;258:177.
[8] Luo HJ, Schülke L, Zheng B. Phys Rev Lett 1998;81:180.
[9] Zheng B, Ren F, Ren H. Phys Rev E 2003;68:046120.
[10] Luo MB, Chen QH, Ying HP, Jiao ZK. Phys Lett A 2002;292:303.
[11] Luo MB, Chen QH, Feng SS, Jiao ZK. J Phys: Condens Matter 2002;14: 6483.
[12] James M. J Phys Chem Solids 2000;61:1865.
[13] Takahashi M, Turek P, Nakazawa Y, Tamura M, Nozawa K, Shiomi D, et al. Phys Rev Lett 1991;67:746.
[14] Clérac R, Miyasaka H, Yamashita M, Coulon C. J Am Chem Soc 2002; 124:12837.
[15] Ung VÂ, Couchman SM, Jeffery JC, McCleverty JA, Ward MD, Totti F, et al. Inorg Chem 1999;38:365.
[16] Bu XH, Liu H, Du M, Zhang L, Guo YM, Shionoya M, et al. Inorg Chem 2002;41:1855.
[17] Pope M, Swenberg CE. Electronic processes in organic crystal and polymers. 2nd ed. New York: Oxford University Press; 1999.
[18] Odegarda GM, Clancyb TC, Gates TS. Polymer 2005;46:553.
[19] Garel T, Orland H, Orlandini E. Eur Phys J B 1999;12:261.
[20] Luo MB, Huang JH. J Chem Phys 2003;119:2439.
[21] Huang JH, Luo MB. Polymer 2004;45:2863.
[22] Feng J, Ruckenstein E. Polymer 2002;43:5775.
[23] Landau DP, Binder K. A guide to Monte Carlo simulations in statistical physics. Cambridge: Cambridge University Press; 2000.
[24] Rysz J. Polymer 2005;46:977.
[25] Lai PK. Phys Rev E 1994;49:5420.
[26] Hu X, Tachiki M. Phys Rev Lett 2000;85:2577.
[27] Hu X, Tachiki M. Phys Rev B 2004;70:64506.
[28] Swendsen RH, Wang JS. Phys Rev Lett 1987;58:86.
[29] Wolff U. Phys Rev Lett 1989;62:361.