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Thermal hysteresis scaling for first-order phase transitions

G P Zheng† and J X Zhang†

Department of Physics, Zhongshan University, GuangZhou, People's Republic of China

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Abstract. We study the effects of time-dependent thermal cycling on the first-order phase transition in cubic Ising systems with four-spin interactions by means of Monte Carlo simulations. The thermal hysteresis or the energy dissipation Q of a thermal cycle can be scaled with respect to the linear heating or cooling rate R: $Q - Q_0 \propto R^b$. We find the exponent b is independent of the interaction strength. $b = 0.47 \pm 0.05$ in an SC lattice while in an FCC lattice and a compressible Ising lattice $b = 0.71 \pm 0.07$, 0.70 ± 0.05 respectively. These simulation results are also compared with the kinetic Ising model and N-vector model in Langevin dynamics.

1. Introduction

In experiments, hysteresis always characterizes a first-order phase transition (FOPT). We can distinguish between hysteresis in two categories. In the first case, there is an equilibrium temperature at which the phase transition takes place, but practically, due to the finite observation time, the order parameter will show hysteretic jumps above and below the transition temperature. This phenomenon reflects the superheating and supercooling, and it is known that the irreversibility is based on the 'ergodic breaking'. In the second case, however, the transition occurs at some spinodal points: it is at these temperatures that the free-energy barrier separating two phases will vanish. The system enters the 'metastable' state prior to its reaching the spinodal points. Recently, scaling of the hysteresis during a first-order phase transition has been of great interest. The simplest case is the field-driven FOPT in magnetic systems [1, 2]. It has been found by some researchers that the magnetic hysteresis can be scaled by the sweeping rate of the external magnetic field [1–5]. The area of hysteresis loop in the conjugate coordinate, i.e., in the M–H frame, indicates the energy loss or energy dissipation during the FOPT. Therefore, the energy dissipation may result, at least to some extent, from the non-equilibrium relaxation of the order parameter of the system under the action of the external driving field.

We now develop this concept of scaling to the thermally driven first-order phase transition. In the time-dependent heating and cooling process, because of the non-equilibrium relaxation of the internal energy (or entropy), the energy dissipation in a thermal cycle may be affected by the feature of thermal cycles, i.e. the starting or the ending temperature points, the amplitude of the temperature oscillation or the rate of variation. Rao and Pandit [4] studied the scaling of the thermal hysteresis for the first time. In their preliminary phenomenological study, they investigated the N-vector model ($(\Phi^2)^3$ model) by using the time-dependent Ginzburg–Landau theory in the large-N limit: they obtained

† Correspondence address: Department of Physics, Zhongshan University, 135 XinGan Road West, 510275 GuangZhou, People's Republic of China. E-mail address: stdp18@zsulink.zsu.edu.cn

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the scaling expression $A \propto r_{1.0}$, where A was the area enclosed by the M–T curve during a thermal cycle and r was the amplitude of the sinusoidal temperature oscillation. In this method, there are two problems they might encounter. Firstly, the amplitude of the temperature oscillation scanning across the transition temperature is small; the paramagnetic phase has not been transformed to a stable ferromagnetic phase and thereafter the spin system is forced to heat to the paramagnetic state. This can bring dramatically history-dependent effects into the phase transition. Secondly, the hysteresis loop area of the M–T curve cannot give the value of energy dissipation during a thermal cycle, which can be easily measured by thermal analysis, e.g., by comparing the DSC measurement of the heat loss and heat absorption during cooling and heating processes.

In order to give a deep insight into this problem, we adopt some Ising models that can show first-order phase transitions by considering the multi-spin interaction. By means of Monte Carlo (MC) simulations, it is possible to study the non-equilibrium aspects of the FOPT in relation to the changes in the thermodynamic conditions. We can quantitatively investigate the relationship between the energy dissipation and the characteristic of the thermal cycle, which can be easily controlled by the Monte Carlo algorithm. In our MC studies, we change the temperature linearly rather than periodically, and the amplitude of thermal sweeping is large enough to ensure the completion of the first-order phase transition, this method of temperature variation is often used by DSC measurements.

2. Models and Monte Carlo simulations

2.1. Ising systems with four-spin interaction

The Ising models with multi-spin interactions were first proposed by Baxter and Wu [6]. In three-dimensional space, the model might show first-order phase transition if four-spin interactions are taken into account [7, 8]. If N spins are placed on the cubic lattice, the Hamiltonian of this type consists of a linear combination of two- and four-spin Ising interactions as follows:

$$\boldsymbol{H} = -J_2 \sum_{\langle i,j \rangle} S_i S_j - J_4 \sum_{\{i,j,k,l\}} S_i S_j S_k S_l - h \sum_i S_i. \tag{1}$$

Here h is the applied magnetic field, $J_2, J_4 > 0$ are the interaction strengths, $S_i = \pm 1$. $\langle\rangle$ indicates the sum extending over the nearest-neighbour spins, and $\{\ \}$ denotes the sum including the spins inside the basic quartets; the basic quartet is defined as an elementary simplex in the cubic lattice. The definitions of the quartets in three cubic lattices (sc, bcc, fcc lattices) are given in [9], and we will use these definitions as references.

Another Ising model with four-spin interactions that is well known for showing an FOPT is the so-called compressible Ising model. The Hamiltonian can be written as

$$\boldsymbol{H} = -J_2 \sum_{\langle i,j \rangle} S_i S_j - (J_4/N) \sum_{\langle i,j \rangle \langle k,l \rangle} S_i S_j S_k S_l - h \sum_i S_i. \tag{2}$$

Here the Hamiltonian differs from (1) only in that $\langle i, j \rangle$ and $\langle k, l \rangle$, which represent every nearest-neighbour pair, are not restricted to form an elementary simplex in the cubic lattice. Their interactions are long ranged.

As indicated by renormalization group analysis [10] and MC simulations [9], the spin systems in cubic lattices governed by Hamiltonian (1) show first-order transitions if $J_2 = 0$; and they might cross over from first order to second order with decreasing ratio J_4/J_2. Furthermore, due to the degeneration of the order states, the systems with pure four-spin interaction will characterize n-component vector models; the order-parameter dimensionality

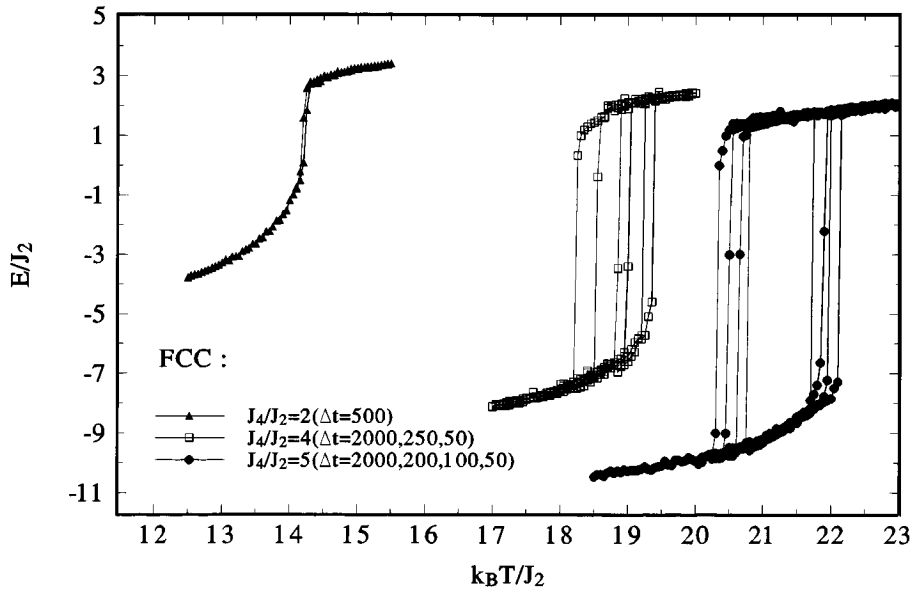

Figure 1. Thermal hysteresis of internal energy at various temperature variation rates in FCC lattice. $\dot{T} = \Delta T/\Delta t$ is indicated by Δt from inner to outer loops. First-order phase transitions at different J_4 are shown. $k_B \Delta T/J_2 = 0.05$.

for body-centred cubic, simple cubic and face-centred cubic systems are $n = 4$, 8 and ∞ respectively. In the compressible Ising model [15], there is an FOPT if $J_4 \neq 0$. Hence the models considered here show a definite FOPT and will give us a convenient way to compare the kinetic phenomenological model and computer experiments. These lead to theoretical insight into the subject we proposed.

2.2. Monte Carlo study

Monte Carlo simulations of hysteresis in FOPTs in spin systems described by Hamiltonians (1) and (2) without the magnetic field are carried out in the conventional way of Metropolis important sampling. The procedure is a simulated heating and cooling method, in which the temperature is increased or decreased with the same interval ΔT. At each temperature the simulations are performed for the same time Δt. The time scale of simulations is given in units of Monte Carlo steps per spin (MCS/spin), corresponding to one lattice spin update. In this simulated annealing method, linear temperature variation is achieved by using the small temperature changes ΔT and a relatively small number of MC steps. Therefore the heating or cooling rate can be measured by $\dot{T} = \Delta T/\Delta t$. We want to stress that because it is our intention to focus on the effects of time-dependent thermal cycling, we should not consider rather long MC running times. However, a long-time Monte Carlo algorithm is needed for this subject, especially for determining the static hysteresis and the initial spin configuration of annealing.

The spin numbers in all the cubic lattices we study are more than $N = 15^3$, and they are all subjected to the periodic boundary conditions with toroidal type. We performed the simulations for some systems of different sizes: no finite-size effects were ever found.

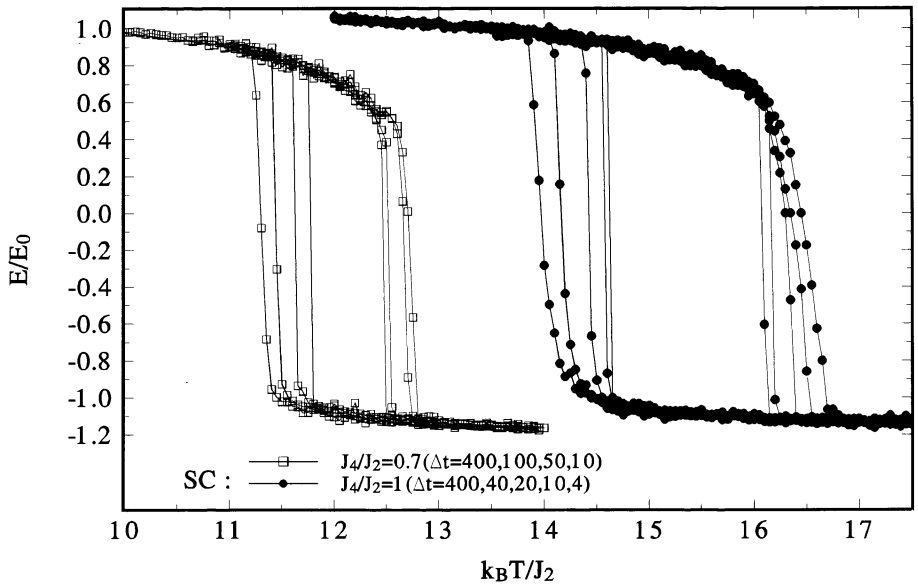

Figure 2. Thermal hysteresis of normalized internal energy at various temperature variation rates in SC lattice. $k_B\Delta T/J_2 = 0.05$. E_0 is the ground state energy.

In the increasing-temperature series, the simulation is started with all the spins setting in the same direction, at a low temperature T_1. In the subsequent constant-temperature ($T = T_i$) simulation, which in all cases lasts Δt (MCS/spin), the simulation is started from the spin configuration obtained from the preceding simulation at temperature $T = T_i - \Delta T$. The simulation is ended at temperature T_2 after the phase transition is terminated. In the decreasing-temperature series, however, there are two kinds of spin configurations with which we can start the simulation. One is the configuration where the spins are chosen randomly, which is the paramagnetic state at infinite temperature; the other is the spin configuration at $T = T_2$, which has been obtained from very slow heating (i.e., $\Delta t > 10^4$). Although the first one is realistic, it must be started at a finite temperature: the error is enormous in the fast annealing process. Therefore we use the configuration at $T = T_2$; furthermore, the temperature is held for a long time: $t_{an} > 10^5$ (MCS/spin). We have checked in our MC studies that no initial-temperature effect is encountered, except in the pure four-spin interaction case ($J_2 = 0$), therefore we will avoid this situation.

The magnetization and internal energy per spin of the systems can be calculated from the following expression:

$$M = \left[\left\langle \sum_i S_i \right\rangle\right]_{av} \Big/ N \qquad E = [\langle H \rangle]_{av}/N. \tag{3}$$

At each T, $\langle\,\rangle$ denotes the thermal average over the last half MC run. The thermal cycles will be repeated two to ten times and the average is denoted by $[\,]_{av}$. The entropy, relative to that at $T = \infty$, can be numerically calculated from the internal energy:

$$S(T) = E(T)/T - \int_0^{1/T} E(T')\,\mathrm{d}(1/T'). \tag{4}$$

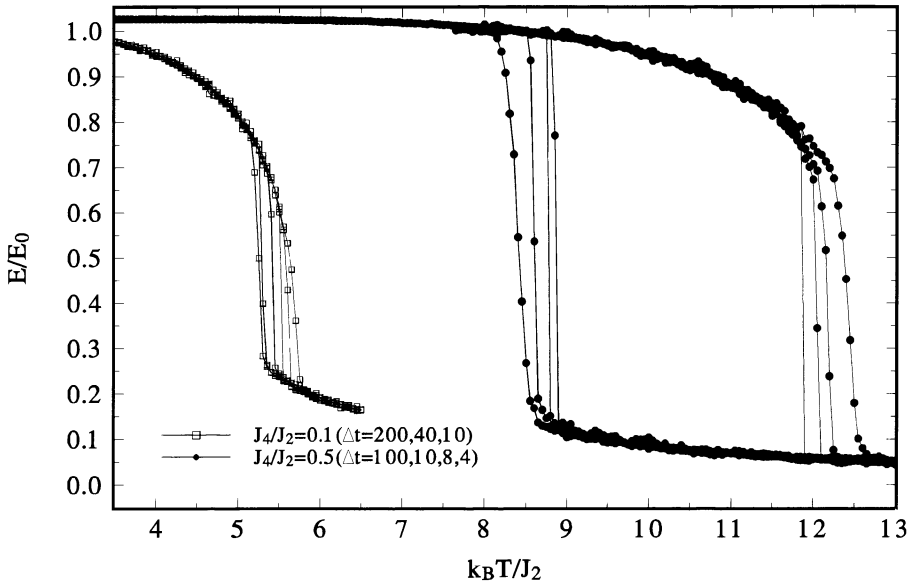

Figure 3. Thermal hysteresis of normalized internal energy at various temperature variation rates in simple cubic compressible Ising lattice. $k_B \Delta T/J_2 = 0.05$.

Therefore the energy dissipation per thermal cycle is

$$Q = \oint T \, \mathrm{d}S. \tag{5}$$

2.3. Results

2.3.1. Thermal hysteresis at different thermal cycle rate. MC simulation for Hamiltonian (1) is firstly done in a very slow thermal cycle. The results are compared with those of the static cases given by Mouritsen *et al* [8, 9]. Although in their simulation the MC steps for some temperatures were dramatically different, especially inside and outside the transition regions, we find our results are analogous to theirs in FCC and SC lattices.

In a face-centred cubic lattice, the number of spins $N = 20^3$. The temperature interval is set to be $k_B \Delta T/J_2 = 0.05$. For a given value of J_4, the heating or cooling rates $\dot{T} = \Delta T/\Delta t$ are measured by MC steps Δt. Because the lifetime of the metastable state is very long, static hysteresis might not be readily obtained even when the temperature variation rate is as small as $\dot{T} = \Delta T/10^4$ (MCS). In order to obtain reasonable thermal hysteresis, the holding time at T_2 must be as long as $t_{an} = 10^6$ (MCS/spin). The variations of internal energy with temperature at various rates are given in figure 1, for different four-spin interaction strengths.

The thermal hysteresis curves for the simple cubic lattice are shown in figure 2. We also simulate the BCC lattice with symmetry-breaking field. Up to a system size of 2×20^3, the fluctuation is so strong that it seems impossible to obtain hysteresis with satisfactory statistical error. Therefore we do not include these MC data.

The same procedure is done for simulating the compressible Ising model in an SC lattice. Figure 3 shows the hysteresis in this spin system.

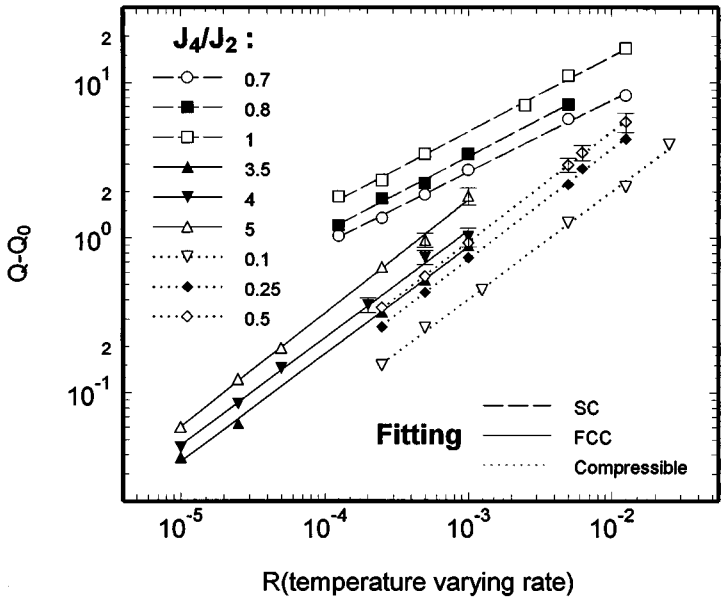

Figure 4. Scaling of energy dissipation with respect to the temperature variation rates in all the cubic lattices with four-spin interactions, at different interaction strengths. Q_0 is static energy dissipation determined by long-time MC simulations. The calculation errors larger than symbol size are indicated by error bars.

2.3.2. Scaling of the thermal hysteresis. The energy dissipation per thermal cycle between T_1 and T_2 can be numerically calculated from equations (4) and (5) at different temperature variation rates, at a fixed value of J_4. The results are shown in figure 4. The energy dissipation per cycle can be scaled as

$$Q = Q_0 + a(\dot{T})^{\beta}. \tag{6}$$

Q_0 is the static energy dissipation of this first-order phase transition, and β is a exponent independent of J_4, within statistical error. We obtain the exponents for SC and FCC lattices $\beta = 0.47 \pm 0.05$ and 0.71 ± 0.07 respectively.

In the compressible Ising lattice, we have the exponent $\beta = 0.70 \pm 0.05$; it is also independent of J_4.

3. Dynamical approach to hysteresis scaling of FOPT

3.1. Kinetic Ising model

In the Glauber type single-spin flip dynamics, the kinetics of a spin S_i is governed by the master equation. In the Glauber stochastic, it can be written as the following equation in S_i [11]:

$$\frac{\mathrm{d}}{\mathrm{d}t}\langle S_i\rangle = -\langle S_i\rangle + \langle \tanh(E_i/k_BT)\rangle \qquad E_i = J_2\sum_j S_j + J_4\sum_{j,k,l} S_jS_kS_l + H. \tag{7}$$

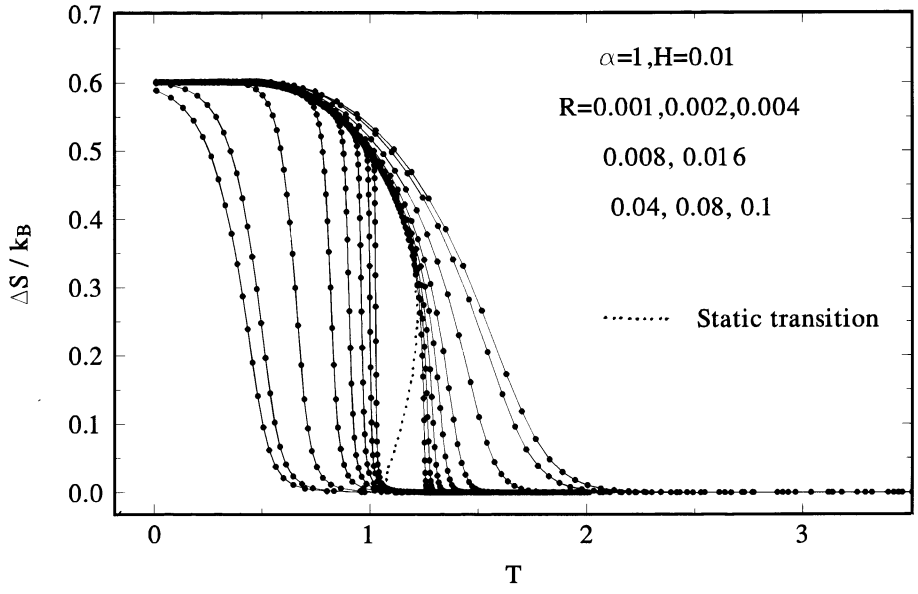

Figure 5. Variation of entropy difference with temperature at different thermal cycle rates R (from inner to outer loops), determined by kinetic Ising model.

Under the mean-field approximation (MFA), the uniform magnetization $M = \langle S_i \rangle$ is independent of i. Therefore we have the equation for $M(t)$:

$$\frac{\mathrm{d}M(t)}{\mathrm{d}t} = -M(t) + \tanh[(M + \alpha M^3 + H)/T]. \tag{8}$$

Here H and T are dimensionless in units of pJ_2 and pJ_2/k_B respectively; p is the number of nearest-neighbour sites; $\alpha = qJ_4/(pJ_2)$ with q the number of basic quartets in cubic lattices. For SC, BCC and FCC lattices, $p = 6$, 8 and 12; $q = 32$, 24 and 8 respectively. In the compressible Ising model, $\alpha = 4J_4/(pJ_2)$.

Equation (8) is solved numerically using fourth and fifth Runge–Kutta formulas, and here we do not discard the magnetic field term, for it is essential for the transition curve on the cooling process. The temperature is varied linearly as $T = T_2 - \dot{T}t$ or $T = T_1 + \dot{T}t$. T_1 and T_2 are well away from the transition temperature, which can be predicted by the MFA [12].

In order to obtain the energy dissipation as in equation (5), we must calculate the entropy from $M(T)$. The entropy of the spin systems is $S = k_B \ln(W)$, where W is the number of spin configurations. Because of the uniform magnetization of the systems $M = \langle S_i \rangle = (1/N) \sum S_i$, we may obtain the relation between the entropy (measured from ground state) and the magnetization, for all the cubic lattices we considered:

$$\Delta S = \tfrac{1}{2} k_B[(1 + M)\ln(1 + M) + (1 - M)\ln(1 - M)]. \tag{9}$$

The variations of the entropy difference with temperature at different temperature variation rates are shown in figure 5. The numerical results are independent of T_1 and T_2. In figure 5, the static transition curve was obtained from equation (8) by setting the left side to zero. According to equation (5), the hysteresis loop area of ΔS–T curves gives the energy dissipation Q per thermal cycle. We notice that at small temperature variation rate, the transitions at increasing and decreasing temperature approach the spinodal points, and Q

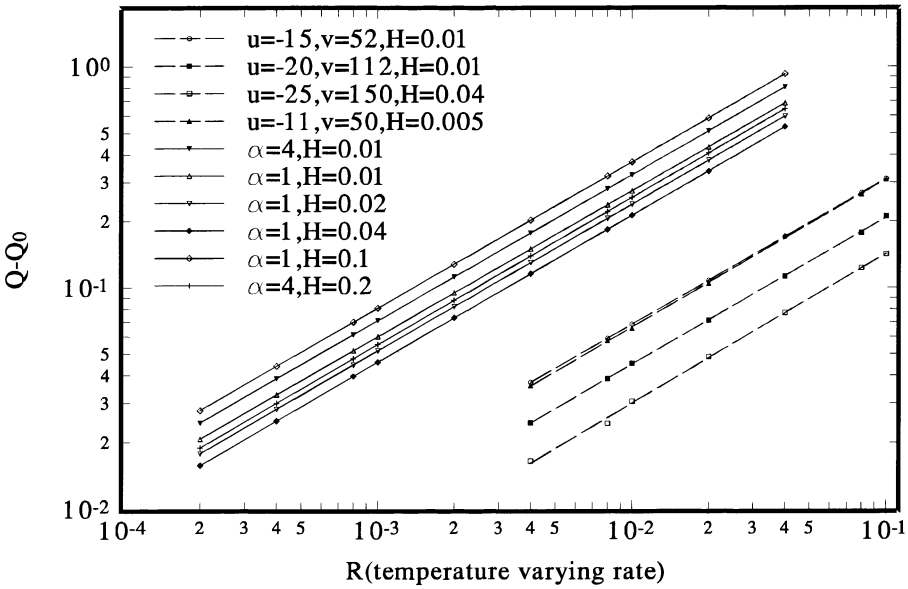

Figure 6. Scaling of energy dissipation at different model parameters: Q_0 is determined from static hysteresis. Solid lines are results of fitting to kinetic Ising model, dashed lines are results of fitting to large-N model.

tends to the static energy dissipation Q_0. Figure 6 shows the difference between Q and Q_0 at various temperature variation rates. It is obvious that the energy dissipation obeys the scaling law (6). The scaling exponent $\beta = 2/3$, independent of the applied field and interaction strength. However, if we scale the hysteresis loop area of M–T curves with respect to the varying rate, there is no definite value of β, though the discrepancy is not very large.

3.2. Langevin dynamics in N-vector model

Let us consider a system described by N-component order parameter $\mathbf{\Phi} = \{\Phi_\alpha(\boldsymbol{r}, t)\}$, $\alpha = 1, \ldots, N$; the Ginzburg–Landau free energy functional of the system can be written as

$$F[\mathbf{\Phi}] = \int \mathrm{d}^d x \left[\frac{1}{2} c \sum_\alpha (\nabla \Phi_\alpha)^2 + U(\mathbf{\Phi}) \right]. \tag{10}$$

Here $U(\mathbf{\Phi}) = (r/2)\mathbf{\Phi}^2 + (u/4N)(\mathbf{\Phi}^2)^2 + (v/6N^2)(\mathbf{\Phi}^2)^3 - N^{1/2}\boldsymbol{H} \cdot \mathbf{\Phi}$. The evolution of the order parameter can be given by the Langevin equation (LE):

$$\partial_t \Phi_\alpha(r, t) = -\frac{\delta F[\mathbf{\Phi}]}{\delta \Phi_\alpha(r, t)} + \Gamma_\alpha(r, t). \tag{11}$$

Γ is the noise and obeys the fluctuation–dissipation theorem:

$$\langle \Gamma_\alpha(x, t) \rangle = 0 \qquad \langle \Gamma_\alpha(r, t) \Gamma_\beta(r', t') \rangle = 2k_B T \delta_{\alpha\beta} \delta(r - r') \delta(t - t'). \tag{12}$$

In large-N limit, LE (11) transforms to the following closed set of equations and can be solved exactly [16, 4]:

$$\frac{\mathrm{d}M(t)}{\mathrm{d}t} = \tfrac{1}{2}(\zeta(t)M(t) + H) \qquad \frac{\partial C(k, t)}{\partial t} = 1 - [k^2 - \zeta(t)]C(k, t) \tag{13}$$

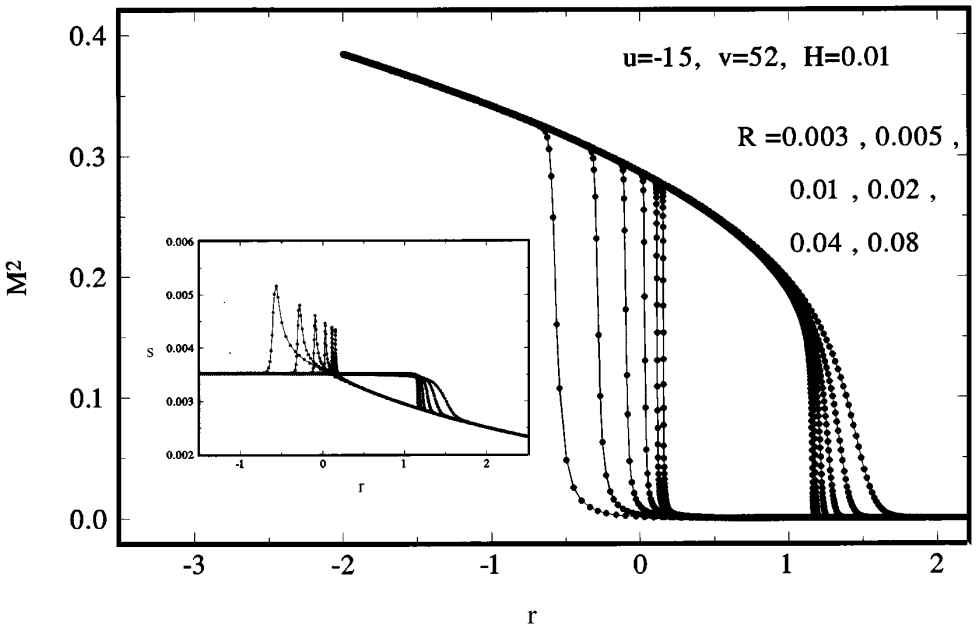

Figure 7. Numerical results of equation (13) at different temperature varying rates R (from inner to outer loops). The inset shows the corresponding structure factor s.

with $\zeta = -(r + us + vs^2 + uM^2 + 2vsM^2 + vM^4)$, $s(t) = K_D \int_0^1 k^{d-1} C(k,t)\,\mathrm{d}k$, where $C(k,t)$ is the Fourier transform of the transverse correlation function. K_D is proportional to the surface area of the unit hypersphere in d-dimensional space [1]; $r \propto T - T_0$, T_0 the critical temperature and u, v are coefficients that result in the FOPT. The detailed numerical method for solving equation (13) at dimensionality $d = 3$ is analogous to those mentioned in the above section.

The energy dissipation can be calculated in equation (5) by using the following relationship: $S(t) \propto \langle \Phi \rangle^2 + \langle \Phi^2 \rangle + a_0 = M^2(t) + s(t) + a_0$. Here we define equilibrium entropy $S = \partial \langle F[\Phi] \rangle / \partial (k_B T)$. $s = \langle \Phi(k,t)\Phi(-k,t) \rangle$ is the structure factor defined in equation (13) and a_0 is constant. Figure 7 is the numerical results of $M^2(t)$ and $s(t)$. We also obtain the scaling expression (6) with the exponent $\beta = 2/3$, as shown in figure 6.

4. Discussion and conclusions

In the above two sections, we demonstrated that the energy dissipation during first-order phase transitions in Ising systems with four-spin interactions could be scaled with respect to the thermal cycle rates; the scaling law was universal for these spin systems in cubic lattices. In our MC studies, we found the exponents were nearly the same in the FCC lattice with local four-spin interactions and the compressible Ising lattice, while they were obviously different from that in the SC lattice with local four-spin interactions: $\beta = 0.47 \pm 0.05$. Using Glauber dynamics and Langevin dynamics for the N-vector model in the large-N limit, we obtained the exponent $2/3$. This confirmed the scaling exponents for the compressible Ising lattice and FCC lattice with local four-spin interactions, but was not valid for predicting the exponent for SC lattices with local four-spin interactions. This might be due to the

strongly fluctuating nature of SC and BCC systems [9, 13, 14], which was suppressed in other systems we had studied and was neglected in the MFA.

In this concept of scaling and universal curves, we scaled the hysteresis loop area of S–T curves, rather than that of the M–T curves. Therefore, the quantities we considered represented the energy dissipation during the first-order phase transitions. Unlike the temperature variation methods in [4], in which the temperature was changed as a cosine function, we decreased and increased the temperature linearly, and the spin systems were well defined as paramagnetic and ferromagnetic states at the low- and high-temperature cycle ends respectively. There were some advantages in using such a temperature variation method. Firstly, the energy dissipation was independent of the initial temperature, therefore we could focus on the effects of cycle rates. Secondly, linear temperature variation is usually used in experiment, especially in DSC measurement, in which thermal dissipation could be accurately measured.

To classify the Ising models we considered here in field theory language, we can describe the systems with pure four-spin interaction as N-component vector models, and construct the Landau–Ginzburg–Wilson free-energy functional. Because of the fluctuations of each parameter component and the couples among them, equations (8) and (13) are not valid to describe the nonequilibrium kinetics of such models. This may result in a scaling exponent different from $2/3$. This issue deserves to be further studied, experimentally and theoretically.

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