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Dynamics of a spin-1 Ising system in the neighborhood of equilibrium states

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The dynamics of a spin-1 Ising system containing biquadratic interactions near equilibrium states is formulated by the method of thermodynamics of irreversible processes. From the expression for the entropy production, generalized forces and fluxes are determined. The kinetic equations are obtained by introducing kinetic coefficients that satisfy the Onsager relation. By solving these equations a set of relaxation times is calculated and examined for temperatures near the phase transition temperatures, with the result that one of the relaxation times approaches infinity near the second-order phase transition temperature on either side, whereas it is sharply cusped at the first-order phase transition temperature. On the other hand, the other relaxation time has a cusp at the second-order phase transition temperature but displays a different behavior at the first-order phase transition, just a jump discontinuity. The behavior of both relaxation times is also investigated at the tricritical point. Moreover, the phase transition behaviors of the relaxation times are also obtained analytically via the critical exponents. Results are compared with conventional kinetic theory in the random-phase or generalized molecular-field approximation and a very good overall agreement is found.

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I. INTRODUCTION

The thermodynamic behavior of many cooperative physical systems can be simulated by the spin-1 Ising model, which is also known as the Blume-Emery-Griffiths model [1]. The model was initially introduced to describe the phase separation and superfluid ordering in ^{3}He-^{4}He mixtures. The equilibrium properties of the model have been studied by well known methods in equilibrium statistical physics such as the mean-field approximation [1–3], effective field theory [4], the Monte Carlo renormalization technique [5], renormalization-group techniques [6], the cluster variation method [7–10], high-temperature series expansion [11], Monte Carlo simulations [12], the constant coupling approximation [13], the transfer matrix method [14], and the linear chain approximation [15]. While the equilibrium properties of the spin-1 Ising model have been studied extensively, the nonequilibrium behavior of the system have not been as thoroughly explored because dynamic models of cooperative phenomena are of more speculative nature.

An early attempt to study the nonequilibrium behavior of the one-dimensional spin-1 Ising system was made by Obokata [16] who used the spin-1 Bethe method but ignored the crystal field, and subsequently extended it into a time-dependent model. Tanaka and Takahashi [17] and also Batten and Lemberg [18] studied the dynamics of a spin-1 Ising model in the molecular-field approximation and also obtained the relaxation curves of order parameters. Saito and Müller-Krumbhaar [19] also investigated the kinetics of a spin-1 antiferromagnetic Ising model using the time-dependent Ginzburg-Landau theory and applied it to crystal growth. Achiam [20] used the real-space renormalization-group approach to study the dynamic behavior of a spin-1 Ising system and found the dynamic exponents. Keskin and co-workers have studied a number of nonequilibrium behaviors of the model [21,22], in particular the ‘‘flatness’’ property of metastable states and the ‘‘overshooting’’ phenomenon as well as the role of unstable states in the phase diagrams, via the path probability method of Kikuchi [23]. Finally, Keskin and Meijer [24] have also investigated the time dependence of the system in the weak coupling limit by a modified version of the Glauber model [25]. But a literature survey leaves us with the impression that the dynamics of the spin-1 Ising model in the neighborhood of equilibrium states have not been investigated in any detail using the methods of nonequilibrium thermodynamics. Onsager's reciprocity theorem [26], deduced by the application of time-reversal symmetry to microscopic fluctuations, can provide some help in evaluating theories for coupled irreversible processes such as relaxation of order parameters in spin systems.

Onsager's relations state that, for thermodynamic forces and fluxes that are linearly related and satisfy a specific set of criteria (to be fully described in Sec. III), the effect of the driving force of each irreversible process upon the rate of the other must be the same. This theorem has been successfully applied to describe the long-time kinetics of many transport or irreversible processes near equilibrium, such as steady-state interface motion during phase transformation in a two-component system [27], transport in inhomegeneous media [28], the gyrothermal effect with polyatomic gases [29], mass and energy flow across the interface between dilute and condensed phases [30], and rarefied gas flows [31].

The purpose of the present paper is, therefore, to formulate the dynamics of the spin-1 Ising system including biquadratic interactions in the neighborhood of thermal equilibrium states and to study the temperature dependence of relaxation times via the ratio of two interaction parameters and the phenomenological kinetic coefficients. In particular, we investigate the behaviors of these times near the phase transition temperatures and the tricritical point. This is achieved by a combination of the thermodynamics of irreversible processes and the equilibrium statistical theory of

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cooperative phenomena. This type of calculation was first performed by Tanaka *et al.* [32]. They studied the relaxation phenomena in a spin-$\frac{1}{2}$ Ising system near the second-order phase transition point. Then Barry [33] and Barry and Harrington [34] created the same problem for an *AB*-type ferromagnetic and antiferromagnetic Ising model, respectively, to investigate the magnetic relaxation near the phase transition temperature.

The remainder of this paper is organized as follows. In Sec. II we give a description of the model and a brief summary of the static properties. In Sec. III, we briefly review Onsager's theorem and derive the kinetic equations. The solution of the kinetic equations near equilibrium states is given in Sec. IV. Finally, a summary and discussion of the results are given in the last section.

II. THE MODEL AND EQUILIBRIUM PROPERTIES

The Hamiltonian of the spin-1 Ising system with bilinear and biquadratic interactions is given by

$$H=-J\sum_{(ij)} S_iS_j-K\sum_{(ij)} Q_iQ_j\,, \tag{1}$$

where the spins located at site *i* on a discrete lattice can take the values 0, ±1. The first term describes the bilinear coupling between the spins at sites *i* and *j* and the second term describes the biquadratic coupling. Both interactions are restricted to the *z* nearest neighbor pair of spins which are absorbed in *J* and *K*. The order parameters of the system are the dipolar order parameter (or magnetization) *S* and the quadrupolar order parameter *Q*, given by

$$S\equiv\langle S_i\rangle, \tag{2}$$

and

$$Q\equiv\langle (S_i)^2\rangle-\tfrac{2}{3}, \tag{3}$$

where $\langle\cdots\rangle$ is the thermal expectation value. The definition given by Eq. (3), which ensures that $Q=0.0$ at infinite temperature, is different from the definition $Q=\langle(S_i)^2\rangle$ used by Blume, Emery, and Griffiths [1] and by Lajzerowicz and Sivardiere [2].

In the molecular-field approximation in the Bragg-Williams formalism, the Helmholtz free energy of the spin-1 Ising system with bilinear and biquadratic interactions is given as

$$F=-NJS^2-NKQ^2-kT\ln W(S,Q), \tag{4}$$

where *N*, *k*, and *T* are the number of Ising spins, the Boltzmann factor, and the absolute temperature, respectively, and $W(S,Q)$ is the number of configurations for given values of dipolar and quadrupolar order parameters. The last term in Eq. (4) is given by

$$\begin{aligned}\ln W(S,Q)=-N[&(\tfrac{1}{3}+\tfrac{1}{2}S+\tfrac{1}{2}Q)\ln(\tfrac{1}{3}+\tfrac{1}{2}S+\tfrac{1}{2}Q)\\&+(\tfrac{1}{3}-Q)\ln(\tfrac{1}{3}-Q)+(\tfrac{1}{3}-\tfrac{1}{2}S+\tfrac{1}{2}Q)\\&\times\ln(\tfrac{1}{3}-\tfrac{1}{2}S+\tfrac{1}{2}Q)].\end{aligned} \tag{5}$$

The equilibrium values of the dipolar order parameter *S* and the quadrupolar order parameter *Q* are found by the conditions

$$\frac{\partial F}{\partial S}=0, \tag{6a}$$

$$\frac{\partial F}{\partial Q}=0. \tag{6b}$$

One can easily find the following set of self-consistent equations by using Eqs. (4), (5), and (6):

$$S=\frac{2e^{2\beta KQ}\sinh(2\beta JS)}{1+2e^{2\beta KQ}\cosh(2\beta JS)}, \tag{7}$$

$$Q=\frac{2}{3}\,\frac{e^{2\beta KQ}\cosh(2\beta JS)-1}{1+e^{2\beta KQ}\cosh(2\beta JS)}, \tag{8}$$

where $\beta=1/kT$. It should be mentioned that Eqs. (7) and (8) can be derived directly (with allowance for the different notation) from the mean-field approximation via the variational principle for the free energy [1] and the lowest approximation of the cluster variational method [9,10]. Since the solution of these equations is discussed extensively in Ref. [35], we shall give only a brief summary here as follows. For $J/K<\frac{1}{3}$ a first-order phase transition occurs to a state with $Q<0.0$ and $S=0.0$, which corresponds to the quadrupolar phase. For $\frac{1}{3}\leqslant J/K<\frac{2}{3}$ there is a first-order phase transition to a state with $S>Q>0.0$, which corresponds to a ferromagnetic phase, and for $J/K\geqslant\frac{2}{3}$ a transition of second order exists to a state with $S>Q>0.0$ in the ferromagnetic phase. The system has a tricritical point for $J/K=\frac{2}{3}$. This information is very important for studying the dynamics of the system.

III. THEORY

A. Summary of the Onsager's reciprocity theorem

In order to state Onsager's theorem, consider a system whose state can be described by a set of independent variables A_i that are even or odd functions of particle velocity. The deviations of these parameters from their equilibrium values are given by

$$\alpha_i=A_i-A_i^0, \tag{9}$$

where A_1^0 is the equilibrium value. At equilibrium the entropy is a maximum and the state variables α_1 are zero by definition. Therefore, for a nonequilibrium state one can write the entropy S_E as

$$S_E = S_E^0 - \frac{1}{2}\sum_{i,j} g_{ij}\alpha_i\alpha_j, \quad (i,j = 1,2,\dots), \tag{10}$$

where S_E^0 is the equilibrium entropy value and g_{ij} are positive definite matrix elements that are called entropy production coefficients and are given by

$$g_{ij} = \left(\frac{\partial^2 S_E}{\partial\alpha_i\partial\alpha_j}\right)_{\text{eq}} = \frac{1}{T}\left(\frac{\partial^2 F}{\partial\alpha_i\partial\alpha_j}\right)_{\text{eq}}. \tag{11}$$

Let the forces X_i and the fluxes J_i be defined as

$$X_i = \frac{\partial S_E}{\partial\alpha_i} = -\sum_j g_{ij}\alpha_j, \tag{12}$$

$$J_i = \frac{d\alpha_i}{dt}. \tag{13}$$

Then, if the forces and fluxes are described by the linear phenomenological equations

$$J_i = \sum_j L_{ij}X_j, \tag{14}$$

Onsager's reciprocity theorem states that

$$L_{ij} = \pm L_{ji}, \tag{15}$$

where the plus sign corresponds to the quantities α_i and α_j having the same parity, and the minus sign corresponds to α_i and α_j having different parity.

B. Derivation of kinetic equations

In order to derive the kinetic equations, let $A_1 = S$ and $A_2 = Q$ be the dipolar and quadrupolar order parameters in the spin-1 Ising system, respectively. Then the deviations of these parameters from their equilibrium values are given by

$$\alpha_1 = \alpha_S = S - S_0 \quad \text{and} \quad \alpha_2 = \alpha_Q = Q - Q_0, \tag{16}$$

where S_0 and Q_0 are the equilibrium values. Using Eq. (10), the entropy for a nonequilibrium state in the system is written as

$$S_E = S_E^0 - \tfrac{1}{2}[g_{SS}(S-S_0)^2 + 2g_{SQ}(S-s_0)(Q-Q_0) + g_{QQ}(Q-Q_0)], \tag{17}$$

with the entropy production coefficients defined by

$$g_{SS} = \frac{1}{T}\left(\frac{\partial^2 F}{\partial S^2}\right)_{\text{eq}} = -Nk\left[\frac{2J}{kT} - \frac{1}{4}\,\frac{\frac{2}{3}+Q_0}{(\frac{1}{3}+\frac{1}{2}S_0+\frac{1}{2}Q_0)(\frac{1}{3}-\frac{1}{2}S_0+\frac{1}{2}Q_0)}\right], \tag{18a}$$

$$g_{SQ} = \frac{1}{T}\left(\frac{\partial^2 F}{\partial S\partial Q}\right)_{\text{eq}} = g_{QS} = \frac{1}{T}\left(\frac{\partial^2 F}{\partial Q\partial S}\right)_{\text{eq}} = -Nk\left[\frac{1}{4}\,\frac{S_0}{(\frac{1}{3}+\frac{1}{2}S_0+\frac{1}{2}Q_0)(\frac{1}{3}-\frac{1}{2}S_0+\frac{1}{2}Q_0)}\right], \tag{18b}$$

$$g_{QQ} = \frac{1}{T}\left(\frac{\partial^2 F}{\partial Q^2}\right)_{\text{eq}} = -Nk\left[\frac{2K}{kT} - \frac{1}{\frac{1}{3}-Q_0} - \frac{1}{4}\,\frac{\frac{2}{3}+Q_0}{(\frac{1}{3}+\frac{1}{2}S_0+\frac{1}{2}Q_0)(\frac{1}{3}-\frac{1}{2}S_0+\frac{1}{2}Q_0)}\right]. \tag{18c}$$

Using Eqs. (9) and (13), we find for the flows in order parameters

$$J_1 = \frac{d\alpha_1}{dt} = J_S = \frac{dS}{dt}, \tag{19a}$$

$$J_2 = \frac{d\alpha_2}{dt} = J_Q = \frac{dQ}{dt}, \tag{19b}$$

and using Eqs. (9)–(12) we have for the forces

$$X_1 = \frac{\partial S_E}{\partial\alpha_1} = X_S = \frac{\partial S_E}{\partial(S-S_0)}, \tag{20a}$$

$$X_2 = \frac{\partial S_E}{\partial\alpha_2} = X_Q = \frac{\partial S_E}{\partial(Q-Q_0)}. \tag{20b}$$

Substituting Eq. (17) into Eqs. (20a) and (20b) one can obtain the forces as

$$X_S = -g_{SS}(S-S_0) - g_{SQ}(Q-Q_0), \tag{21a}$$

$$X_Q = -g_{SQ}(S-S_0) - g_{QQ}(Q-Q_0). \tag{21b}$$

According to the Onsager theory of irreversible thermodynamics, the linear relations between the currents and forces given by Eq. (14) may be written in terms of a matrix of phenomenological rate coefficients where the off-diagonal elements are the negatives one of another across the main diagonal (the matrix is not symmetric since S is an odd variable while Q is an even variable under time inversion):

$$\begin{bmatrix} J_S \\ J_Q \end{bmatrix} = \begin{bmatrix} L_S & -L \\ L & L_Q \end{bmatrix}\begin{bmatrix} X_S \\ X_Q \end{bmatrix}. \tag{22}$$

Substituting Eqs. (21a) and (21b) into Eq. (22) and using Eqs. (19), we obtain the kinetic equations as

$$\frac{dS}{dt} = -(L_S g_{SS} - L g_{SQ})(S-S_0) - (L_S g_{SQ} - L g_{QQ})(Q-Q_0), \tag{23a}$$

$$\frac{dQ}{dt} = -(Lg_{SS}+L_Q g_{SQ})(S-S_0) - (L_Q g_{QQ}+Lg_{SQ})(Q-Q_0). \tag{23b}$$

The solutions of these kinetic equations are given in the next section.

IV. SOLUTION OF THE KINETIC EQUATIONS NEAR EQUILIBRIUM STATES

In order to study the dynamics of the model in the neighborhood of equilibrium states, a solution of the form $e^{-t/\tau}$ is assumed for the linearized kinetic equations given by Eqs. (23a) and (23b) and the approaches of $S(t)$ and $Q(t)$ to their equilibrium values are described by two characteristic times, which are also called the relaxation times. Therefore, to find these times requires the solution of the secular equation

$$\begin{vmatrix} \tau^{-1}-L_S g_{SS}+Lg_{SQ} & -L_S g_{SQ}+Lg_{QQ} \\ -Lg_{SS}-L_Q g_{SQ} & \tau^{-1}-L_Q g_{QQ}-Lg_{SQ} \end{vmatrix} = 0, \tag{24}$$

which yields the following two inverse relaxation times:

$$\frac{1}{\tau_1} = \frac{(g_{SS}g_{QQ}-g_{SQ}^2)(L_S L_Q+L^2)}{L_Q g_{QQ}+L_S g_{SS}}, \tag{25a}$$

$$\frac{1}{\tau_2} = (L_Q g_{QQ}+L_S g_{SS})\left(1-\frac{(g_{SS}g_{QQ}-g_{SQ}^2)(L_S L_Q+L^2)}{(L_Q g_{QQ}+L_S g_{SS})^2}\right). \tag{25b}$$

One observes that the off-diagonal rate coefficient L coupling the dipolar and quadrupolar order currents in Eq. (22) appears in Eqs. (25a) and (25b) only through the factor $(L_S L_Q+L^2)$. The assumption is made in this paper that L^2 is negligible compared with $L_S L_Q$ for temperatures close to the critical temperature T_C, i.e.,

$$L_S L_Q+L^2 \approx L_S L_Q, \tag{26}$$

for temperatures near T_C. Strickly speaking, assumption (26) may be completely verified only by a theory external to irreversible thermodynamics [33]. The dipolar and quadrupolar order parameters S and Q approach their equilibrium values S_0 and Q_0 with two reduced characteristic times τ_1 and τ_2 given by Eqs. (25a) and (25b).

The behavior of these relaxation times near the phase transition points can be obtained analytically from the critical exponents. As one approaches the critical point, various thermodynamic functions may diverge or go to zero or even remain finite. It is therefore convenient to introduce an expansion parameter

$$\epsilon = T_C - T, \tag{27}$$

where T_C is the critical temperature, which is a measure of the distance from the critical point. Near the critical point, the relaxation times, namely, Eqs. (25a) and (25b), can be written in the form

$$\tau_1(\epsilon) = \frac{L_S g_{SS}+L_Q g_{QQ}}{(L_S L_Q+L^2)(g_{SS}g_{QQ}-g_{SQ}^2)}, \tag{28a}$$

$$\tau_2(\epsilon) = \frac{L_S g_{SS}+L_Q g_{QQ}}{(L_S g_{SS}+L_Q g_{QQ})^2-(L_S L_Q+L^2)(g_{SS}g_{QQ}-g_{SQ}^2)}, \tag{28b}$$

where the entropy production coefficients become

$$g_{SS}(\epsilon) = -Nk\left[\frac{2J}{k(T_C-\epsilon)} - \frac{1}{4}\,\frac{\frac{2}{3}+Q_0}{(\frac{1}{3}+\frac{1}{2}S_0+\frac{1}{2}Q_0)(\frac{1}{3}-\frac{1}{2}S_0+\frac{1}{2}Q_0)}\right], \tag{29a}$$

$$g_{SQ}(\epsilon) = g_{QS}(\epsilon) = -Nk\left[\frac{1}{4}\,\frac{S_0}{(\frac{1}{3}+\frac{1}{2}S_0+\frac{1}{2}Q_0)(\frac{1}{3}-\frac{1}{2}S_0+\frac{1}{2}Q_0)}\right], \tag{29b}$$

$$g_{QQ}(\epsilon) = -Nk\left[\frac{2K}{k(T_C-\epsilon)} - \frac{1}{\frac{1}{3}-Q_0} - \frac{1}{4}\,\frac{\frac{2}{3}+Q_0}{(\frac{1}{3}+\frac{1}{2}S_0+\frac{1}{2}Q_0)(\frac{1}{3}-\frac{1}{2}S_0+\frac{1}{2}Q_0)}\right]. \tag{29c}$$

The equilibrium values of the order parameters appearing in Eq. (29) can be expressed in the vicinity of T_C by

$$S_0(\epsilon) \cong 2\left[\frac{k}{2K}\,\frac{3J/K-1}{(3J/K-2)J/K}\right]^{1/2}\epsilon^{1/2}, \tag{30a}$$

$$Q_0(\epsilon) \cong \frac{k}{2K}\,\frac{3}{3J/K-2}\,\epsilon \tag{30b}$$

for $J/K > \frac{2}{3}$ where the system undergoes a second-order phase transition and

$$S_0(\epsilon) \cong \left(\frac{k}{2K}\,\frac{40}{13}\right)^{1/4}\epsilon^{1/4}, \tag{31a}$$

$$Q_0(\epsilon) \cong \left(\frac{k}{2K}\,\frac{10}{13}\right)^{1/2}\epsilon^{1/2} \tag{31b}$$

for the tricritical point $J/K = \frac{2}{3}$. For $\frac{1}{3} < J/K < \frac{2}{3}$, where the system undergoes a first-order phase transition, each of them vanishes at T_C as

$$S_0(\epsilon) \cong 2\left[\frac{k}{2K}\,\frac{3J/K-1}{(2-3J/K)J/K}\right]^{1/2}(-\epsilon)^{1/2}, \tag{32a}$$

$$Q_0(\epsilon)\cong\frac{k}{2K}\,\frac{3}{2-3J/K}(-\epsilon). \tag{32b}$$

The critical exponents for the functions $\tau_1(\epsilon)$ and $\tau_2(\epsilon)$ are defined, respectively, as

$$\lambda_1=\lim_{\epsilon\to 0}\frac{\ln\tau_1(\epsilon)}{\ln\epsilon}, \tag{33a}$$

$$\lambda_2=\lim_{\epsilon\to 0}\frac{\ln\tau_2(\epsilon)}{\ln\epsilon}, \tag{33b}$$

This definition is valid for all values of λ_i $(i=1,2)$, the negative values corresponding to divergences of the variables $\tau_1(\epsilon)$ and $\tau_2(\epsilon)$ as ϵ goes to zero, the positive values corresponding to relaxation times that approach zero, and the zero values corresponding to logarithmic divergence, jump singularities, or cusps (the relaxation times are finite at the critical point but one of their derivatives diverges) [36]. On the other hand, in order to distinguish a cusp from a logarithmic divergence another sort of critical exponent (λ') is introduced. To find the exponent λ' that describes the singular parts of the functions $\tau_1(\epsilon)$ and $\tau_2(\epsilon)$ with a cusplike singularity, we first find the smallest integer j such that the derivatives $\partial^j\tau_1/\partial\epsilon^j=\tau_1^{(j)}(\epsilon)$ and $\partial^j\tau_2/\partial\epsilon^j=\tau_2^{(j)}(\epsilon)$ diverge as $\epsilon\to 0$ [36]. We then define

$$\lambda_i'=j+\lim_{\epsilon\to 0}\frac{\ln|\tau_i^{(j)}(\epsilon)|}{\ln\epsilon}\quad (i=1,2). \tag{34}$$

Using Eqs. (29)–(32) in Eq. (28) and substituting the resulting expression into Eqs. (33) one can calculate the critical exponents for the relaxation times at the phase transition temperatures.

The behavior of the relaxation time τ_1 as a function of the temperature in the ferromagnetic phase is shown in Figs. 1(a)–1(c) for several values of J/K, which correspond to the second-order phase transition temperature, the first-order phase transition temperature, and the tricritical point, respectively. In the figures, the solid curves are for $L_S=10$, $L=0.000\,01$, $L_Q=1.0$, the dashed curves for $L_S=15$, $L=0.000\,01$, $L_Q=1.5$, and the numbers associated with each curve are the various values of J/K. The vertical dotted lines refer to the phase transition temperatures. In this case, τ_1 increases rapidly with increasing temperature and diverges as the temperature approaches the second-order phase transition point on either side, as seen in Fig. 1(a), because the critical exponents of τ_1 in the ferromagnetic phase for $J/K>\frac{2}{3}$ are found to be $\lambda_1=-1.0$ for all kinetic coefficients. On the other hand, τ_1 also increases rapidly as the temperature is raised but makes a sharp cusp with a critical point exponent $\lambda_1=0.0$ but $\lambda_1'=1.0$ (since the second derivative of τ_1 diverges as ϵ^{-1}) at the first-order phase transition temperature, illustrated in Fig. 1(b). It should be mentioned that this is a truly first-order behavior and not due to the proximity of critical behavior via a tricritical point. Moreover, the behavior of τ_1 as a function of temperature near the tricritical point

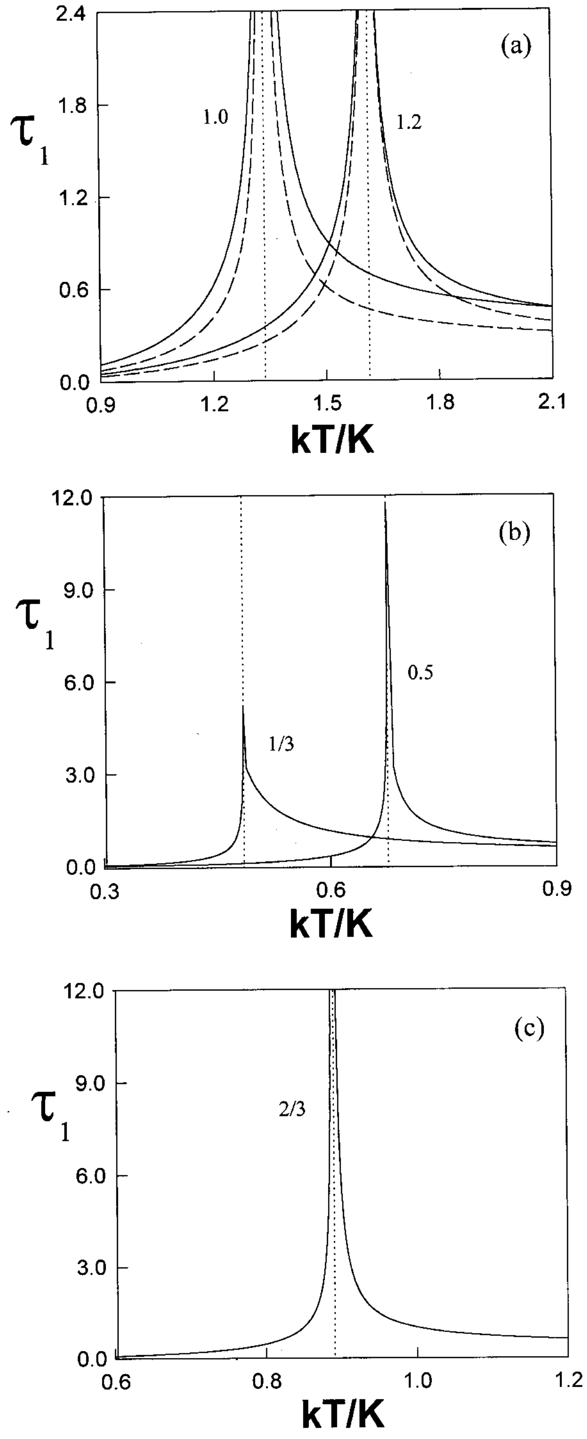

FIG. 1. (a) Relaxation time τ_1 as a function of the temperature for the ferromagnetic phase. The number accompanying each curve denotes the value of J/K. The vertical dotted lines represent the critical points, which are all second order. The solid and dashed curves correspond to $L_S=10$, $L=0.00001$, $L_Q=1.0$ and $L_S=15$, $L=0.00001$, $L_Q=1.5$, respectively. (b) Same as (a) but the system undergoes a first-order ferromagnetic phase transition and the vertical dotted lines indicate the first-order phase transition temperatures. $L_S=10$, $L=0.0001$, $L_Q=1.0$. (c) Same as (a) but for the system at the tricritical point and $L_S=10$, $L=0.00001$, $L_Q=1.0$.

is plotted in Fig. 1(c). One can see from the figure that τ_1 also increases rapidly with temperature and diverges at the tricritical point as in the second-order case but with a different value of critical exponent, namely, $\lambda_1 \approx -0.893$. Since the critical exponent for the tricritical case is smaller than that for the critical case the divergence for τ_1 near the tricritical point is more sudden than near the second-order phase transition point. Furthermore, τ_1 remains constant very far from the phase transition temperatures and tricritical point. Finally, we have found that increasing the values of L_S and L_Q leads to a speeding up of the whole relaxation process as can be seen by comparing the dashed and solid curves in Fig. 1(a).

The dependence of the other relaxation time τ_2 on the temperature in the case of the ferromagnetic phase is represented in Figs. 2(a)–2(c) for several values of J/K, which correspond to the second-order phase transition temperature, the first-order phase transition temperature, and the tricritical point, respectively. In these figures, the solid and dashed curves correspond to $L_S = 10$, $L = 0.000\,01$, $L_Q = 1.0$ and $L_S = 15$, $L = 0.000\,01$, $L_Q = 1.5$, respectively, and the numbers on the curves are the values of J/K. The vertical dotted lines illustrate the critical temperatures. τ_2 scarcely varies with temperature in this phase, and slightly increases just below and above the phase transition temperatures. It should be stressed that cusps occurred for τ_2 at the critical and tricritical points, seen in Fig. 2(a) and Fig. 2(c), respectively, because the second derivative of τ_2 for the critical case and the first derivative for the tricritical case diverge as ϵ^{-1} and as $\epsilon^{-1/2}$, respectively, when $\epsilon \rightarrow 0$. Hence from Eq. (34) it follows that $\lambda_2' = 2 - 1 = 1$ for the critical case and $\lambda_2' = 1 - \frac{1}{2} = 0.5$ for the tricritical case. On the other hand, τ_2 displays a different behavior at the first-order phase transition temperature, just a jump discontinuity with $\lambda_2 \approx 0.0$ [see Fig. 2(b)]. We have also found that increasing values of L_S and L_Q leads to a speeding of the whole relaxation process [compare also the dashed and solid curves in Fig. 2(a)].

The temperature dependence of the relaxation times τ_1 and τ_2 in the quadrupolar phase is shown in Fig. 3 for several values of J/K, which correspond to the first-order phase transition temperature. In the figure, τ_1 is depicted as solid curves and τ_2 as dashed curves for only one case, namely, $L_S = 10$, $L = 0.000\,01$, and $L_Q = 1.0$. The number accompanying each curve denotes the value of J/K and the dotted line corresponds to the first-order phase transition temperature in the quadrupolar order parameter. Unlike the relaxation time τ_1 in the ferromagnetic phase, τ_1 in the quadrupolar phase does not depend on J/K below the critical temperature, whereas it depends on J/K above the critical point. It increases rapidly with increasing temperature but remains finite at the critical point. On the other hand, the other relaxation time τ_2 scarcely varies except at temperatures just below and above the first-order phase transition temperature, where it increases slightly with increasing J/K.

Phenomenological insight can be given into the different behaviors of the relaxation times via the corresponding eigenvectors of the secular equation, namely, Eq. (24). The eigenvectors $\phi_{(k)}$ $(k = 1,2)$, are determined from the following equation:

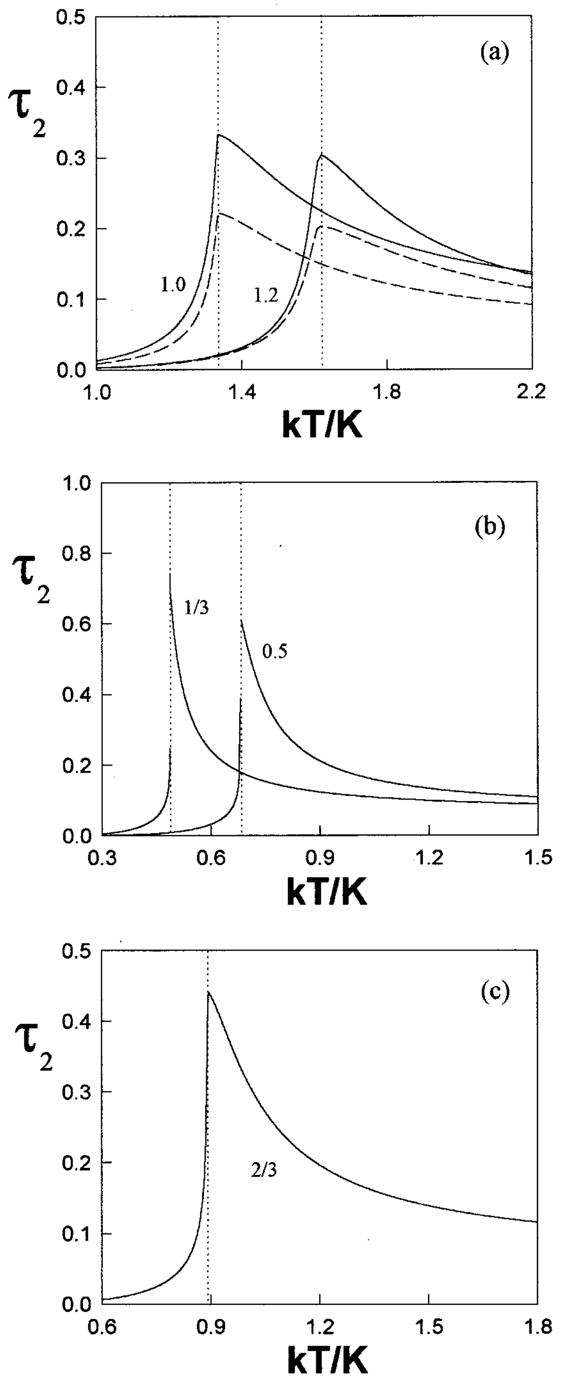

FIG. 2. (a) Same as Fig. 1(a), but for the relaxation time τ_2. (b) Same as Fig. 1(b), but for the relaxation time τ_2. (c) Same as Fig. 1(c), but for the relaxation time τ_2.

$$\begin{bmatrix} \tau_k^{-1} - L_S g_{SS} + L g_{SQ} & -L_S g_{SQ} + L g_{QQ} \\ -L g_{SS} - L_Q g_{SQ} & \tau_k^{-1} - L_Q g_{QQ} - L g_{SQ} \end{bmatrix} \begin{bmatrix} \phi_{(k)1} \\ \phi_{(k)2} \end{bmatrix} = 0, \tag{35}$$

where τ_k^{-1} are the eigenvalues given by Eq. (25). Equation (35) yields the pair of equations

$$(\tau_k^{-1} - L_S g_{SS} + L g_{SQ}) \phi_{(k)1} + (-L_S g_{SQ} + L g_{QQ}) \phi_{(k)2} = 0, \tag{36a}$$

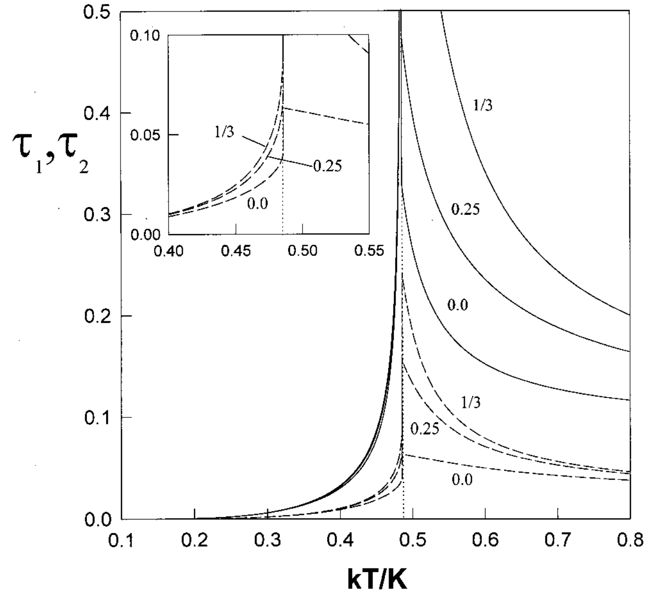

FIG. 3. Relaxation times τ_1 and τ_2 as functions of temperature for the quadrupolar phase. The number accompanying each curve denotes the value of J/K. The vertical dotted line represents the critical point, which is first order and the same for each J/K. The solid and dashed curves correspond to τ_1 and τ_2, respectively, and $L_S=10$, $L=0.00001$, $L_Q=1.0$.

$$(-Lg_{SS}-L_Q g_{SQ})\phi_{(k)1}+(\tau_k^{-1}-L_Q g_{QQ}+Lg_{SQ})\phi_{(k)2}=0. \tag{36b}$$

Arbitrarily, we let $\phi_{(k)1}=1$. Then

$$\phi_{(k)2}=\frac{-\tau_k^{-1}+L_S g_{SS}-Lg_{SQ}}{-L_S g_{SQ}+Lg_{QQ}} \tag{37a}$$

or

$$\phi_{(k)2}=\frac{Lg_{SS}+L_Q g_{SQ}}{\tau_k^{-1}-L_Q g_{QQ}-Lg_{SQ}}. \tag{37b}$$

Hence, the corresponding eigenvectors are

$$\phi_{(k)}=\begin{bmatrix}1\\ \phi_{(k)2}\end{bmatrix}. \tag{38}$$

Having found the system of relaxation times and the corresponding eigenvectors, it is instructive to calculate next the normal coordinates associated with the negative reciprocals of these relaxation times and the eigenvectors. Diagonalizing the system of equations (23) one finds

$$\begin{bmatrix}\dot{Y}_1\\ \dot{Y}_2\end{bmatrix}=-\begin{bmatrix}\tau_1^{-1} & 0\\ 0 & \tau_2^{-1}\end{bmatrix}\begin{bmatrix}Y_1\\ Y_2\end{bmatrix}, \tag{39}$$

where Y_1 and Y_2 are the normal coordinates. Y_1 and Y_2 are obtained by using Eq. (38) as

$$Y_1=(S-S_0)-\frac{\tau_1^{-1}-L_S g_{SS}+Lg_{SQ}}{Lg_{QQ}-L_S g_{SQ}}(Q-Q_0), \tag{40a}$$

$$Y_2=(S-S_0)-\frac{\tau_2^{-1}-L_S g_{SS}+Lg_{SQ}}{Lg_{QQ}-L_S g_{SQ}}(Q-Q_0). \tag{40b}$$

Using Eq. (40), the dipolar and quadrupolar order parameters may be written, respectively, as

$$S=S_0+\frac{1}{\tau_2^{-1}-\tau_1^{-1}}\{[\tau_2^{-1}+\tfrac{1}{2}(Lg_{SQ}-L_S g_{SS})]Y_1 -[\tau_1^{-1}+\tfrac{1}{2}(Lg_{SQ}-L_S g_{SS})]Y_2\}, \tag{41a}$$

$$Q=Q_0+\frac{1}{\tau_2^{-1}-\tau_1^{-1}}(Lg_{QQ}-L_S g_{SQ})(Y_1-Y_2). \tag{41b}$$

Equations (41) show that the relaxation of the dipolar and quadrupolar order parameters is characterized by both relaxation times τ_1 and τ_2. For temperatures near the critical temperatures T_C, Y_2 decays much more rapidly in time than Y_1 since τ_1 increases rapidly and approaches infinity while τ_2 increases only slightly for such temperatures. Therefore, one concludes that both of the order parameters given by Eq. (41) experience a critical slowing down. It should be mentioned that, for temperatures near T_C, not only (as mentioned above) does Y_1 decay much more slowly in time than Y_2 but also Eq. (41a) shows that the amplitude of the normal coordinate Y_2 is much smaller than the amplitude of the normal coordinate Y_1. These behaviors have also been observed in the theory of relaxation phenomena in Ising antiferromagnets [34]. On the other hand, if the temperature is near the first-order phase transition temperature, Y_1 decays more rapidly than Y_1 in the case of the second-order phase transition temperature, because τ_1 increases rapidly but does not approach infinity at the first-order phase transition. Moreover, Y_2 behaves just like Y_2 in the case of a second-order phase transition.

V. SUMMARY AND DISCUSSIONS

In this paper, we have studied the dynamics of the spin-1 Ising system containing biquadratic interactions in the neighborhood of thermal equilibrium states by means of Onsager's theory of irreversible thermodynamics. More specifically, using an expression for the free energy obtained by the molecular-field approximation in the Bragg-Williams formalism, the entropy produced in the irreversible process is calculated and the time derivatives of dipolar and quadrupolar order parameters are treated as fluxes conjugate to their appropriate forces in the sense of Onsager's theory. The kinetic equations are obtained by introducing the phenomenological kinetic coefficients that satisfy the Onsager reciprocal relation. The solution of these equations near equilibrium states is given by two relaxation times which describe the nonequilibrium behavior in the cooperative system. The behavior of these relaxation times as a function of temperature is determined and examined for temperatures near the phase transition points. The results are summarized as follows. One of the relaxation times (τ_1) increases rapidly with increasing temperature and tends to infinity near the critical point as $(T_C-T)^{-1}$ and the tricritical point as $(T_C-T)^{-0.893}$, but it has a sharp cusp with $\lambda_1'=1$ at the first-order phase transition point in the ferromagnetic phase. The other relaxation time (τ_2) scarcely varies with temperature in the ferromagnetic phase; it increases slightly just below and above the phase transition temperatures and the tricritical point. It should be noted that cusps are seen for the critical and tricritical behaviors of τ_2 with $\lambda_2'=1$ and $\lambda_2'=0.5$, respectively, while a jump discontinuity ($\lambda_2=0.0$) is observed for the first-order behavior of τ_2. On the other hand, in the quadrupolar phase, τ_1 increases rapidly with increasing temperature, remains finite at the first-order phase transition, and does not depend on J/K below the critical points, whereas it depends on J/K above the critical points. However, like τ_2 in the ferromagnetig phase, τ_2 in the quadrupolar phase also scarcely varies with temperature and slightly increases just below and above the first-order phase transition point. Moreover, we also give phenomenological insight into the different behaviors of the relaxation times, via the corresponding eigenvectors of the secular equation.

The behavior of the relaxation times as a function of temperature mentioned above is also compared with the results of conventional kinetic theory in the random-phase or generalized molecular-field approximation [17] and exactly the same behavior is found for τ_1 and τ_2 (compare Figs. 1 and 2 here with Fig. 2 in Ref. [17], and also Fig. 3 here with Fig. 1 in the same reference). It is worthwhile to mention that the relaxation times above the critical temperatures are not obtained in Ref. [17].

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