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Dynamic Behavior of a Spin-1 Ising Model. I. Relaxation of Order Parameters and the "Flatness" Property of Metastable States

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The dynamic behavior of a spin-1 Ising system with arbitrary bilinear and biquadratic pair interactions is studied by using the path probability method, and approaches of the system toward the stable or metastable equilibrium states according to the ratio of interaction parameters and rate constants are presented. In particular, we investigate the relaxation of the order parameters for temperatures less than, equal to, and greater than the second-order and first-order phase transitions. From this investigation, the "flatness" property of metastable states is seen explicitly. We also show how a system freezes in a metastable state as well as how it escapes from one metastable state to the other.

KEY WORDS: Spin-1 Ising system; path probability method; metastable states; relaxation curves.

1. INTRODUCTION

The spin-1 Ising model (also known as the Blume–Emery–Griffiths model) has served has a paradigm for a large number of physically important phenomena. The first studied[1] in the context of superfludity and phase separation in $He^3 - He^4$ mixtures. Then the model has been extented to study condensation and solidification of a simple fluid as well as binary fluids,[2] tricritical points in binary and tenary fluids,[3] microemulsions,[4] semiconductor alloys,[5] electronic conduction models,[6] magnetic materials,[7] the re-entrant phenomenon in phase diagrams,[8] critical behavior

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and multicritical phase diagrams,[9–12] study of metastable and unstable states,[13–15] intermetallic alloys.[16] The above works were done by the well known methods in the equilibrium statistical physics.

While the statistics of the spin-1 Ising systems have been studied extensively, the dynamics of the spin-1 Ising systems have not been as thorougly explored. An early attemps to study dynamics of one-dimensional spin-1 Ising system was made by Obokata[17] who used the spin-1 Bethe method and subsequently extented it into a time-dependent model. Tanaka and Takahashi,[18] and also Batten and Lemberg,[19] studied dynamics of the spin-1 Ising system in the molecular field approximation and obtained the relaxation curves of order parameters. Saito and Müller-Krumbhaar[20] investigated the kinetics of a spin-1 antiferromagnetic Ising model using the time-dependent Ginzburg-Landau theory. Achiam[21] used the real space renormalizasyon-group approach to study the critical relaxation of the one-dimensional spin-1 Ising model. Keskin and Meijer[22–23] and Keskin *et al.*[24] have also studied a number of nonequilibrium behavior, especially the role of the unstable states in phase diagrams, of a spin-1 Ising system via the path probability method of Kikuchi.[25] Recently, Keskin and Meijer[26] studied the time-dependent one-dimensional spin-1 Ising system by means of the modified version of Glauber's one-dimensional spin relaxation model.

In this paper we give a treatment of the dynamics of a spin-1 Ising model with arbitrary bilinear and biquadratic pair interactions using the path probability method[25] and study approaches of the system toward the stable or metastable equilibrium states according to the ratio of two interaction parameters and rate constants. Particularly we investigate the relaxation of the order parameters for temperatures less than, equal to and greater than the second-order and first-order phase transitions. From this investigation, the "flatness" property of the metastable states is seen explicitly. We also examine how the system relaxes in metastable states hence becomes frozen-in in the nonequilibrium states, or escapes to other metastable state.

The structure of this paper is as follows: In sec. 2 the model and the static properties are presented briefly. Sec. 3 contains the derivation of the dynamic equations and their solutions. Finally the discussion of the results and summary are given in the last section.

2. THE MODEL AND THE STATIC PROPERTIES

The spin-1 Ising system is a three-state and two-order parameter system. The average value of each of the spin state will be indicated X_1, X_2 and X_3 which are also called the state or spin variables. X_1 is the fraction

of spins value $+1$, X_2 is the fraction of spins that have the value 0, and X_3 is the fraction of spins that have the value -1, and X_i obeys the normalization relation. Two order parameters are introduced as follows: (1) the average magnetization $\langle S\rangle$, (2) the quadrupole moment Q which is a linear function of the average squared magnetization $\langle S^2\rangle$, written as

$$Q \equiv 3\langle S^2\rangle - 2 \tag{1}$$

The order parameters can be expressed in terms of the internal variables are given by

$$S \equiv \langle S\rangle = X_1 - X_3, \qquad Q = \langle Q\rangle = X_1 - 2X_2 + X_3 \tag{2}$$

We consider the spin-1 Ising system where spins interact with each other by the following Hamiltonian

$$H = -\sum_{\langle kl\rangle} \tfrac{1}{2}(JS_kS_l + KQ_kQ_l) \tag{3}$$

where $S_k = +1, 0, -1$ at each lattice site k, Q_k is a quadrupole operator defined by Eq. (1), and $\langle kl\rangle$ indicates summation over all pairs of nearest-neighbor sites. J is the bilinear exchange interaction and K is the biquadratic exchange interaction.

Using the lowest approximation of the cluster variation method,[27] the free energy F can be found as

$$-\frac{F}{N} = \frac{1}{2}JS^2 + \frac{1}{2}KQ^2 - k_BT\sum_{i=1}^{3} X_i(\ln X_i - 1) + \lambda\left(1 - \sum_{i=1}^{3} X_i\right) \tag{4}$$

where λ is introduced to maintain the normalization condition, N is the number of lattice points, k_B is the Boltzmann factor and T is the absolute temperature.

The minimization of Eq. (4) with respect to X_i and using Eq. (2), gives the set of self-consistent equations

$$\begin{aligned} S &= \frac{2\,\mathrm{Sinh}(\alpha KS/k_BT)}{\exp(-3KQ/k_BT) + 2\,\mathrm{Cosh}(\alpha KS/k_BT)} \\ Q &= \frac{\mathrm{Cosh}(\alpha KS/k_BT) - \exp(-3KQ/k_BT)}{\mathrm{Cosh}(\alpha KS/k_BT) + (1/2)\exp(-3KQ/k_BT)} \end{aligned} \tag{5}$$

where $\alpha = J/K$ is called the ratio of the coupling constants or the relative energy barrier.

These two nonlinear algebraic equations are solved by using the Newton–Raphson method and thermal variations of S and Q for several values of α are plotted in Fig. 1. Since the solution of these equations and the figure are discussed in Refs. 13, 24 extensively, we shall only give a brief summary here. In the figure, subscript 1 indicates the stable solutions (drawn lines), 2 the metastable solutions (dashed-dotted lines) and 3 the unstable solutions (dashed lines). This classification is done by comparing the free energy values of these solutions and as well as investigating to the free energy surfaces. The stable states correspond to the lowest minimum, the metastable states to the secondary or local minimum and the unstable states correspond to the saddle point or the peak in the free energy surfaces. T_l, T_u are the lower and upper limit of stability temperature, respectively. T_{tr} is the first order phase transition temperature. It should be also mentioned that for $\alpha \geqslant 6$ a second order phase transition exists, for $3 \leqslant \alpha < 6$ a first order phase transition occurs and for $\alpha < 3$ there is a first order transition in Q with $Q < 0$ and so $S = 0$. The system has a tricritical point for $\alpha = 6$. These information are very important for the studying of relaxation of order parameters.

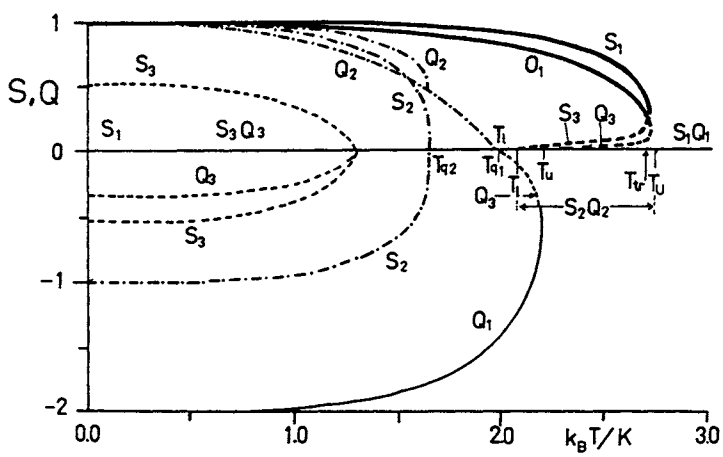


Fig. 1. The order parameters S and Q as functions of reduced temperature, exhibiting a first-order phase transition. Subscript 1 indicates the stable states (drawn lines), 2 the metastable state (dashed-dotted lines) and 3 the unstable states (dashed lines) T_l and T_u are the lower and upper limit of stability temperatures, respectively, T_{qi} the quasicritical temperature and T_{tr} is the first order phase transition temperature. Heavy lines are for $\alpha = 4.0$ and thin lines for $\alpha = 2.0$.

3. DERIVATION OF DYNAMIC EQUATIONS AND THEIR SOLUTIONS FAR FROM EQUILIBRIUM

In this section we derive the dynamic or rate equations by using the path probability method (PPM).[25] In this method the rate of change of the state variables is written as

$$\frac{dX_j}{dt} = \sum_{i \neq j} (\mathbb{X}_{ij} - \mathbb{X}_{ji}) \tag{6}$$

where $\mathbb{X}_{ij}$ is the path probability rate for the system to go from state i to j. Detailed balancing requires that

$$\mathbb{X}_{ij} = \mathbb{X}_{ji} \tag{7}$$

Two options were introduced for $\mathbb{X}_{ij}$ by Kikuchi[25] and he called recipes I and II. We use recipe II, namely

$$\mathbb{X}_{ij} = k_{ij} Z^{-1} X_i \exp\left(-\frac{\partial E}{\partial X_i}\right) \tag{8}$$

where k_{ij} is the rate constants with $k_{ij} = k_{ji}$, Z is the partition function and E is the internal energy of the system, can be found working out Eq. (3) and given in Eq. (4). Z are calculated by using Eq. (3) and found

$$Z = \sum_{i=1}^{3} e_i \qquad (i = 1, 2, 3) \tag{9}$$

where

$$e_1 = e^{[(JS + KQ)/k_B T]},\ e_2 = e^{[(-2KQ)/k_B T]},\ e_3 = e^{[(-JS + KQ)/k_B T]} \tag{10}$$

There are two rate constants in this model as follows: the first rate constants $k_{12} = k_{23} = k_1$ which is the insertion or removal of particles associated with the translational of particles through the lattice and the second rate constant $k_{13} = k_2$ is associated with reorientation of a molecule at a fixed site in the language of a lattice gas. Since the time interval of Δt is taken small enough, double process, the simultaneous insertion, removal or rotation of two particles do not take place, i.e. only single jumps are allowed.

Using Eqs. (2), (6) and (8), the dynamic equations for the order parameters are found:

$$\frac{Z}{k_1}\frac{dS}{dt} = -(ke_1 + e_2 + ke_3) - \frac{1}{3}(1-k)(e_1 - e_3)\,Q + \frac{2k+1}{3}(e_1 - e_3)$$

$$\frac{Z}{k_1}\frac{dQ}{dt} = -(e_1 + e_2 + e_3)\,Q + (e_1 - 2e_2 + e_3)$$

where $k = k_2/k_1$, Z and e_i are given Eqs. (9) and (10) respectively.

In order to study the relaxation which occurs from states far from the equilibrium, it is necessary to solve these dynamic equations. We solve these dynamic equations by using the Runge–Kutta method. Relaxation curves of order parameters for several values of α, k_i and k_BT/K are plotted in Figs. 2–4. The discussion of these solutions will be given in the next section.

4. DISCUSSION OF RESULTS AND SUMMARY

Relaxation proceses which occur in the spin-1 Ising system with arbitrary bilinear and biquadratic pair interactions are treated by using the PPM. Especially we study the relaxation of the order parameters to illustrate the "flatness" property of the metastable state. In order to study the relaxation which occurs far from equilibrium states, it is necessary to solve the dynamic equations, which are derived using the PPM. The solutions are given in Figs. 2–4 for several values of α, k_i and k_BT/K.

Figure 2 shows the relaxation of the order parameters for the temperatures less than and greater than the second order phase transition. From this case, the following results have been concluded: (1) If the temperature is less than the second order phase transition temperature, the system always relaxes to the stable states. Therefore relaxation processes are independent of the rate constants and initial values of order parameters, seen as heavy lines in Fig. 2. (2) If the initial conditions are chosen near the point to the total order, and the temperature is equal to and greater than the critical temperature, system relaxes into disordered states (thin lines in Fig. 2). It should be noticed that if the temperature is equal to the critical temperature, the system takes too long time to relax into disorder states. On the other hand, if the temperature is greater than the critical temperature, it takes short time to relax into disorder states. This behavior has been also observed in a time dependent one-dimensional spin-1/2 Ising system[28] by using the Glauber model.[29] (3) Increasing value of the rotational rate constant, k_2, leads to a speed-up of the whole relaxation process. The reason for choosing $k_2 > k_1$ is that most systems have a shorter relaxation time for a rotation than for a transition.

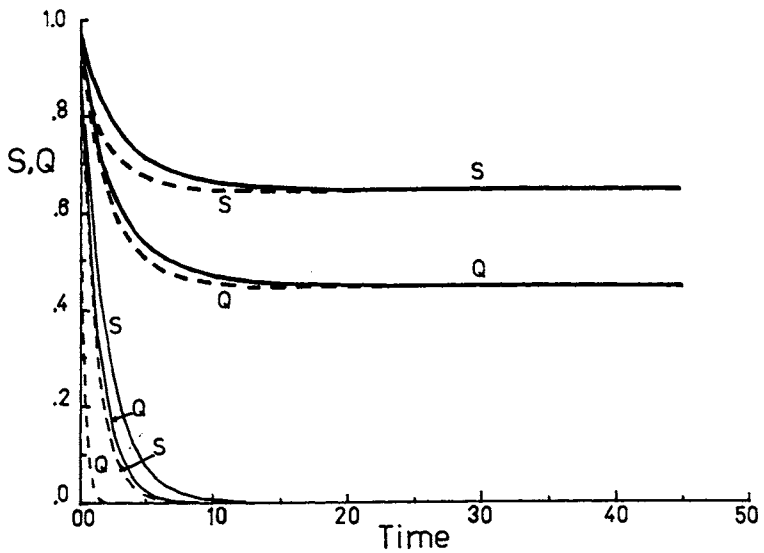


Fig. 2. Relaxation curves of the order parameters S and Q for two different sets of values of the rate constants: $k_1 = k_2 = 1$ (solid) and $k_1 = 1$ and $k_2 = 10$ (dashed), $\alpha = 7.5$ ($k_B T_C/K = 5.0$). Subscript i indicates the initial values. Heavy lines are for $k_B T/K = 4.5$, $S_i = 0.999$ and $Q_i = 0.999$ and thin lines for $k_B T/K = 10$, $S_i = 0.999$ and $Q_i = 0.999$.

Figure 3 illustrates the relaxation of the order parameters in which the first order phase transition takes place. In this case, the behavior of the relaxation of order parameters is found similar to the Fig. 2 for the temperature smaller than, equal to and greater than the first order phase transition temperature. However, if the temperature is between T_u and T_l, the upper and lower limit of stability temperature, the relaxation processes are different. For example, if $\alpha = 4.0$ and $k_B T/K = 2.695$ and initial values of S are greater than their unstable solutions S_3 and initial values of Q are near Q_3, the system always relaxes into stable states, e.g. seen in Fig. 3a (heavy lines). Nevertheless, if initial value of Q is greater than its unstable solutions Q_3 and S is smaller than its unstable solution S_3, the system relaxes into the stable states for $k_1 = 1$ and $k_2 = 10$, but for $k_1 = k_2 = 1$ the system into a metastable state, namely $S = 0.000$ and $Q = 0.000$, hence frozen-in in the metastable state, illustrated thin lines in Fig. 3a. Flat regions of the relaxation curves ($S = 0.000$ and $Q = 0.000$), do not correspond to the lowest minimum, are metastable states. Because one of the characterization of a metastable state is a "flatness" property of relaxation curves.[30] In our previous works, we also showed that $S = 0.000$ and $Q = 0.000$ state which is between T_u and T_1, is a metastable state because this state corresponds

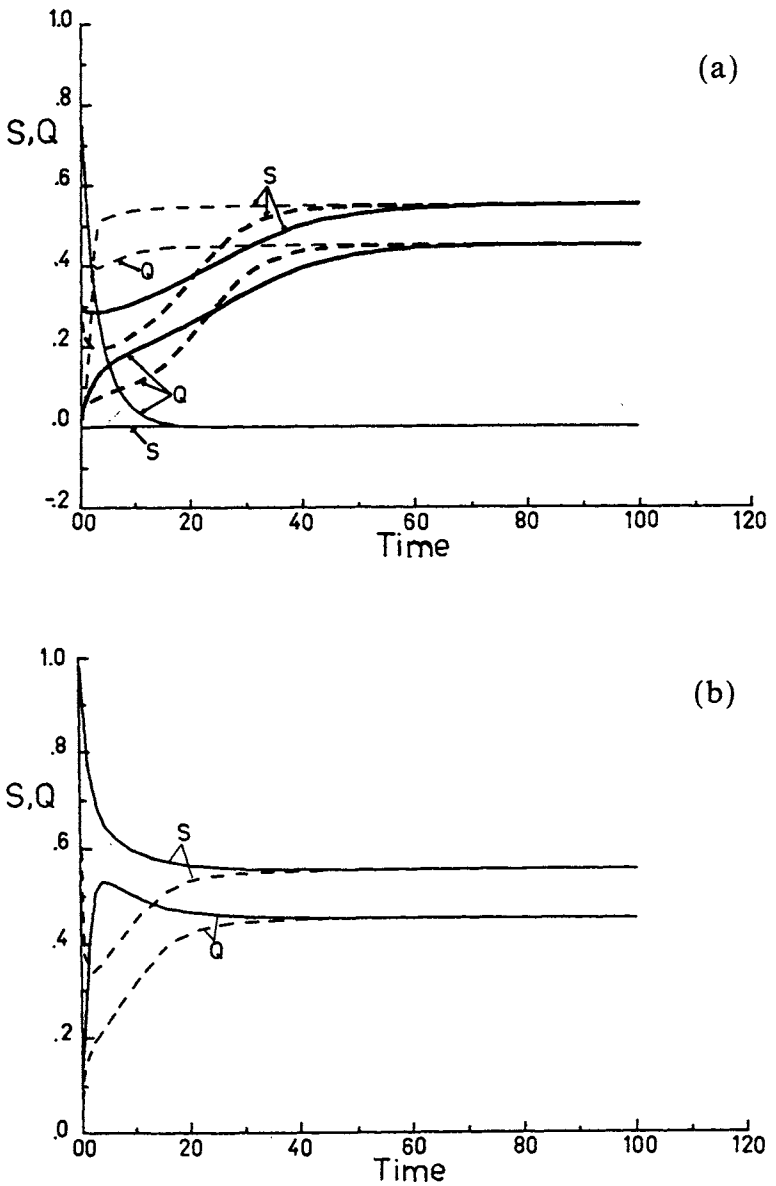
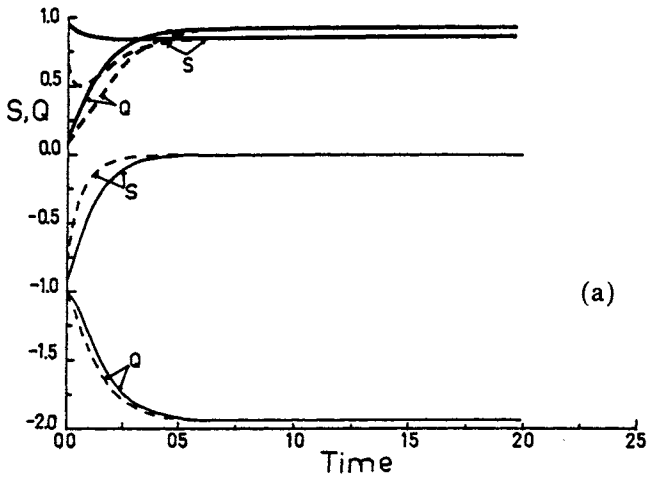


Fig. 3. Same as Fig. 2 but $\alpha = 4.0$ and $k_B T/K = 2.695$. Subscript i indicates the initial value, s the stable state and m the metastable state. (a) Heavy lines are for $S_i = 0.3$ and $Q_i = 0.001$ ($S_s = 0.550$ and $Q_s = 0.451$) and thin lines for $S_i = 0.0001$ and $Q_i = 0.999$ ($S_s = 0.550$, $Q_s = 0.451$, $S_m = 0.000$ and $Q_m = 0.000$). (b) $S_i = 0.999$ and $Q_i = 0.001$ ($S_s = 0.550$ and $Q_s = 0.451$).

to secondary or local minimum in the contour map of the free energy surfaces.[13, 14] This fact was also illustrated by using the flow diagrams which show the solution of dynamic equations in two dimensional phase space of S and Q.[24] On the other hand, for the initial value of S is greater than its unstable solution S_3 and Q is greater than Q_3 the system always relaxes into stable state, as seen in Fig. 3b. Moreover, in this case since we have also unstable states, for a number of cases the system tries to go to unstable state via one of the order parameters, but after sometime the relaxation curve makes a sharp turn (a U-turn so to speak or inverse U-turn, seen in the figures) and relaxes to either stable states (in most cases) or to metastable states (in a few cases). This called "overshooting" phenomenon which is often discussed in glass transition and also has been observed in a number of other systems.[31, 32] It should be noticed that if both initial values of S and Q are smaller than their unstable solutions, the system always relaxes into the metastable state.

Figure 4 is obtained for $\alpha = 2$ and it shows the most interesting relaxation processes. In this case there is a first order phase transition in Q with $Q < 0$ and so $S = 0$, and the system has more than one metastable and unstable states (see also thin lines in Fig. 1). If the initial values of S and Q are chosen near one of their metastable states, the system relaxes into one of the metastable states (namely, $S_m = 0.856$ and $Q_m = 0.924$), seen as heavy lines in Fig. 4a, otherwise into the stable state ($S_m = 0.000$ and $Q_m = -1.940$), illustrated thin lines in Fig. 4a. On the other hand, if the initial value of S is near one of its metastable states, but Q is far from one of the metastable states the system relaxes into one of the metastable states (namely, $S_m = -0.856$ and $Q_m = 0.924$) for $k_1 = k_2 = 1$, but it relaxes into the stable state for $k_1 = 1$ and $k_2 = 10$, heavy lines in Fig. 4b. It is worthwhile to mention that the "overshooting" phenomenon is also seen in this case.

The other interesting result which we find and illustrate in Fig. 4b with thin lines. In the figure there are two flat regions on the relaxation curves. These flat regions are the metastable state, because they do not correspond to the lowest free energy value. We obtain this figure, for initial values of S and Q are equal to zero, $k_B T/K = 1.55$, $k_1 = k_2 = 1$ and also $k_1 = 1$, $k_2 = 10$. In this case, the system first relaxes into one of the metastable state where $S_{1m} = 0.000$ and $Q_{1m} = 0.580$ which corresponds the first flat region on relaxation curves. Then after some time the system escapes from it and relaxes to the other metastable state where $S_{2m} = 0.587$ and $Q_{2m} = 0.754$ which corresponds to the second flat region on the relaxation curves. Hence the system frozen-in in this second metastable state. These flat regions do not correspond to the lowest minimum of free energy, therefore they are metastable states. We have also shown that these states are



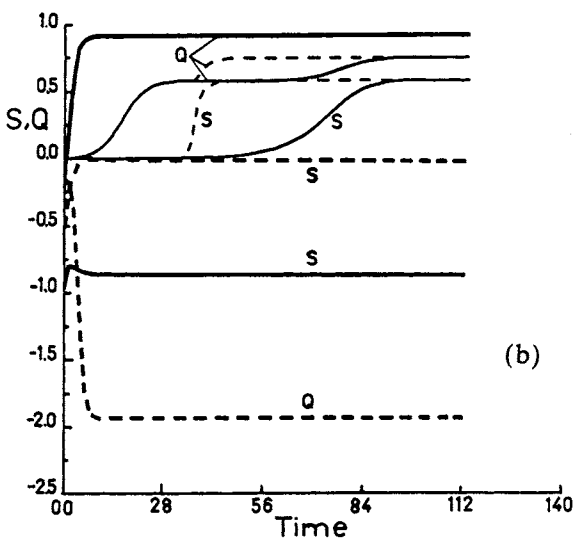


Fig. 4. Same as Fig. 3 but $\alpha = 2.0$. (a) Heavy lines are for $k_B T/K = 1.25$, $S_i = 0.999$ and $Q_i = 0.01$ ($S_m = 0.856$ and $Q_m = 0.924$) and thin lines for $k_B T/K = 1.25$, $S_i = -0.999$ and $Q_i = -0.999$ ($S_s = 0.000$ and $Q_s = -1.940$). (b) Heavy lines are for $k_B T/K = 1.25$, $S_i = -0.999$ and $Q_i = -0.25$ ($S_s = 0.000$, $Q_s = -1.940$ and $S_m = -0.856$, $Q_m = 0.924$) and thin lines for $k_B T/K = 1.55$, $S_i = 0.000$ and $Q_i = 0.000$ ($S_{1m} = 0.000$, $Q_{1m} = 0.580$ and $S_{2m} = 0.587$, $Q_{2m} = 0.857$. Subscript $1\,m$ indicates the first metastable state, $2m$ the second metastable state).

metastable states by using the different methods such as the contour map of free energy surfaces[13] and the flow diagrams which illustrate the solution of dynamic equations in two dimensional phase space of S and Q.[24] Finally, we should also mention that this figure also helps us to see how a system escapes from one metastable state to the other. The phenomenon of escaping from one metastable to the other is found in the review paper of Hanggi *et al.*[33]

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