Metastable states of an Ising-like thermally bistable system

Isidor Shteto, Kamel Boukheddaden, and François Varret
Laboratoire de Magnétisme et d'Optique, CNRS-Université de Versailles/St. Quentin en Yvelines, 45 Avenue des Etats Unis, F78035 Versailles Cedex, France

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The lifetimes of the metastable states are investigated in an Ising-like model associated with thermally bistable systems. A discrete mesoscopic Markovian dynamic is established using an optimized version of the previously presented Monte Carlo entropic sampling method. This is well suited to an extensive study of the role of the physical parameters: temperature, interaction parameter, electronic energy gap. By combining a discrete Markovian mesoscopic dynamic and the absorbing Markov chain technique, we obtain an analytical access to the average lifetime of the metastable state. One-variable and two-variable approximations for the original microscopic master equation are presented and discussed. A typical difference in the thermal dependence of the lifetime of the low- and the high-temperature metastable states is found, and explained as a consequence of the temperature-dependent field associated with the Ising-like model. The validity, the advantages, and the limits of the method are discussed, as well as the possible consequences on the behavior of spin transition systems. A prospective for a possible phenomenological finite-size scaling is presented.
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I. INTRODUCTION

Bistable systems are those that present two phases on experimental time scales. From the strict thermodynamic point of view, one of these phases is stable (equilibrium state) and the other one is metastable (quasiequilibrium state); they are associated respectively with an absolute and a secondary minimum of the free energy in the configurational space. The most familiar examples are supercooled vapor, ferromagnet with magnetization opposite to the applied field, or phase separation of alloys. These phenomena may involve first-order transition with hysteresis. The system initially trapped in a metastable state escapes (returns to the stable state) through thermal by activated processes. In other words, the energy fluctuations of the system highly govern the lifetime of the metastable state.

The metastable states have been the object of many studies [1–4]. Indeed, their understanding represents a practical interest, e.g., for the lifetimes of memory devices, as well as a basic interest. In almost all real systems metastable states have finite lifetimes [5], i.e., are essentially kinetic. Being a nonequilibrium phenomenon, the time evolution of a microscopic system in a metastable state is described stochastically, in terms of master or Focker-Planck equations. In the general case, i.e., that of the interacting systems, there is no analytical solution for the above equations. Also, mean-field, Glauber-like approaches are not suited because they miss the fluctuations needed for the escape from the metastable state. Finally, Monte Carlo simulations in principle provide an exact resolution of the microscopic equations, but the numerical procedure is obviously far too slow with respect to the magnitude of lifetimes in most of real systems.

Theories for the metastable lifetimes have been proposed on the basis of physical models, beginning from the classical nucleation theory of Becker-Döring, [6] up to the field theoretical theory of Langer [7–10]. The classical nucleation theory yields only qualitative results, because it cannot account for configurational entropy. The Langer theory provides correct analytical expressions for the nucleation rate of continuous systems. Even though its validity is doubtful for discrete systems, it was successfully tested for the square lattice Ising system under a field at sufficiently high temperatures [11].

Recently, Lee *et al.* [12] adapted the standard formalism of projection operators to the microscopic Markovian master equation, in order to calculate the lifetime of metastable states. The *projection operator formalism* [13–15] reduces the number of variables without loss of information, i.e., the reduced equation is an exact transformed form of the original one. But, in compensation, the initial Markovianity of the evolution is generally lost, i.e., the projected equation contains memory terms. However, Lee *et al.* suggested to drop the memory terms as long as the metastability of the system is strong. This approximation, which leads to a simple discrete time evolution equation for macroscopic distribution functions, will be used and discussed in the present work. The choice and the number of the macroscopic variables will also be discussed.

The success of this approach depends on the calculation of macroscopic probability distributions at equilibrium, which is already possible for small systems, thanks to the development of appropriate new Monte Carlo sampling methods [16–19]. Indeed, we recently improved the original Monte Carlo entropic sampling algorithm introduced by Lee [17], expressed in terms of density of states sampling. We optimized it in order to access to larger size systems [16–19]. The sampled density of states provides the complete distribution functions at equilibrium; i.e., it implicitly contains the fluctuations needed for calculating the lifetimes of the metastable states. Once the density of states sampling has been performed, in reduced macroscopic variables, then all distribution probabilities, for any set of parameter values (temperature, interaction parameter, energy gap) can be derived analytically. This analytical character confers the den-

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sity of states method a great advantage with respect to other sampling methods (see Ref. [16]).

In this way, for the example of an Ising model, Lee *et al.* showed that the macroscopic Markovian dynamics is very successful (i.e., compares quite well with the simulations in Metropolis dynamic) in calculating the mean lifetime of metastable states. This was implicitly supported by our previous work [18], where the relaxation paths from the metastable state were projected on the surface of a two-variable macroscopic distribution. An excellent agreement between the macroscopic Markovian path, the line of greater equilibrium probability and the mean dynamic Metropolis path was obtained.

In the present work, we deal with the Ising-like case, i.e., the general situation of the two-level systems, with an energy gap and different degeneracies. It is worth remarking that the relaxation from a metastable state has been widely studied for non-temperature-driven, first-order transitions, such as the classical Ising model under a field [20–22,11,12]. In the present work we focus on thermally bistable systems, which undergo first-order transitions, and develop metastable states under the variation of temperature, the other external constraints being kept constant. A common aspect that affects the metastability in these systems is that the temperature plays a double role: it is both the ''inner'' driving mechanism of the phase transition (through its effects on the free energy barriers), and the source of the fluctuations which activates the relaxation.

Among the multitude of such systems, going from the q-state Potts model, biquadratic (Blume-Capel or BEG [23]) models to glassy or disordered systems, we are interested in a very simple case: the Ising-like, short-range interactions system. It is equivalently described as an Ising system under an effective field, which varies linearly with temperature. Such a model [24,25] successfully describes the spin-crossover phenomena, and is considered here to be representative of the thermally bistable systems. [These phenomena arise in molecular iron (II) complexes at the solid state. Such a molecule presents two spin states (high spin and low spin) with different degeneracies, associated with different vibrational properties in the two spin states separated by a energy gap Δ. The cooperative interaction between the spin crossover molecules leads to a first-order transition with hysteresis loops (see Ref. [26]).] It is taken here in the simple case of an isotropic nearest-neighbor Ising square lattice under a temperature-dependent effective field.

This paper is organized as follows. In Sec. II the equilibrium properties of the Ising-like model are reviewed. Section III contains a brief review of the works related to the dynamics near the first-order transitions, i.e., the dynamics of metastable states; the validity of Langer's field theoretical model is reviewed in detail. In Sec. IV the projection operator method is formulated and discussed; a comparison between one-variable and two-variable approximations is made and commented in Sec. IV C. In Sec. V some results obtained for the metastable lifetimes of the short-ranged Ising-like system are presented; in Sec. V C these results are commented in relation to their incidence on spin-transition systems. Section VII contains a general discussion and some perspectives.

II. ISING-LIKE MODEL FOR THERMALLY BISTABLE SYSTEMS: STATIC ASPECTS

The model we consider here was first introduced by Wajnflasz and Pick [24] for molecular spin transition. It is an Ising-like Hamiltonian, having the same expression as the classic Ising model under a field Δ. However, the eigenstates are degenerate and have different degeneracies. The Ising-like Hamiltonian is [24]

$$\mathcal{H}=-J\sum_{\langle i,j\rangle} s_i s_j+\tfrac{1}{2}\Delta\sum_i s_i, \tag{2.1}$$

where s_i, s_j have eigenvalues of $+1,-1$ with respective degeneracies g_+, g_-. In terms of equilibrium probabilities (or from the partition function form) it is easily shown that this system is equivalent to a classical (nondegenerated) Ising model under a temperature-dependent effective field [27]:

$$h_{\text{eff}}=\Delta-\frac{1}{\beta}\ln g \tag{2.2}$$

with $\beta=(1/kT)$ and $g=(g_+/g_-)$. Then, the Ising-like Hamiltonian is written as

$$\mathcal{H}_0=-\sum_{\langle i,j\rangle} J_{i,j}s_i s_j+\tfrac{1}{2}\sum_i\left(\Delta_i-\frac{1}{\beta}\ln g\right)s_i. \tag{2.3}$$

The mean-field treatment of the problem classically follows and leads to the reduced Hamiltonian per site

$$\frac{\mathcal{H}_0}{zJ}=[-m+\tfrac{1}{2}(d-rt)]s_i \tag{2.4}$$

with the dimensionless parameters d, r, and t defined as

$$\left\{\begin{array}{l} d=\dfrac{\Delta}{zJ} \\ r=\ln g \\ t=\dfrac{k_B T}{zJ}\end{array}\right\}, \tag{2.5}$$

where z is the number of first neighbors and $m=\langle s\rangle$ the averaged ''magnetization'' per spin, which in our problem only denotes the difference between the fractions of molecules in the high-spin and low-spin states.

The reduced free energy and the corresponding self-consistent equations are then easily derived as follows:

$$f=\frac{\mathcal{F}}{NzJ}=\frac{1}{2}m^2-t\ln\left[2g\cosh\left(\frac{m+\frac{1}{2}(-d+rt)}{t}\right)\right], \tag{2.6}$$

$$m=\tanh\left(\frac{m+\frac{1}{2}(-d+rt)}{t}\right). \tag{2.7}$$

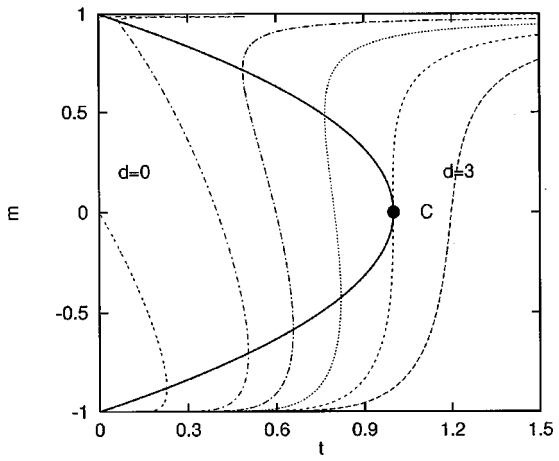

FIG. 1. Hysteresis loops in the (m,t) plane where $t=k_BT/zJ$ is the dimensionless reduced temperature. These curves are calculated using Eq. (2.8) for $r=2.5$. The energy gap values, in reduced units, are from left to right: $d=0$, 1, 1.5, 2.0, 2.5 (critical value: $d_c=r$) and 3. The parts of the curves with a negative slope dm/dt, correspond to unstable equilibrium states. The full line curve is the spinodal curve, i.e., the limit of instability area. C is the critical point $(t_C=1,\ m_c=0,\ d_C=r)$.

This is immediately identified to the well-known self-consistent equation of spins-$\frac{1}{2}$ under a field. Equation (2.7) can be inverted in temperature and then be written as follows:

$$t=\frac{d-2m}{r-\ln\dfrac{1+m}{1-m}}. \tag{2.8}$$

The temperature dependence of the magnetization is given by Eq. (2.8) for m restricted in the [0,1] interval. The obtained curves are shown in Fig. 1. They exhibit first-order transitions which are explained by noting that the effective field $d_{\text{eff}}=d-rt$, temperature-dependent, changes its sign at $t_{\text{eq}}=d/r$, which is the transition temperature. This is similar to the classical Ising model under a field: the negative (positive) magnetization stable state is obtained at low (high) temperatures, due to the negative (positive) effective field.

Different behaviors of the model in Fig. 1 are reviewed, showing both first-order transitions and simple conversions according to the values of Δ, r, and J, as well as a critical temperature $T_C=zJ$. The spinodal curve is obtained by solving the equation $\partial t/\partial m=0$. This illustrates the strong similitudes between the behaviors of this model and the phase diagram of the liquid-gas transition. For further analysis of the Ising-like model, see Ref. [27].

From this mean-field treatment, the first-order transition develops only if the equilibrium temperature T_{eq} is located below the critical temperature T_C. Even though this is a mean-field result, we think that it is not less than an exact result, as long as the existence of a first-order transition in a field h (located at the $h=0$) is rigorously proven for the Ising model, at subcritical temperatures. In fact, a mathematical singularity of the free energy is observed at $h=0$, for the Ising model under a field, at subcritical temperatures [28,29]. It seems evident that the above observation would be immediately transposed for the Ising-like model considered here: that is, the temperature-driven, first-order transition should develop as long as the temperature where the effective field vanishes stays below the exact critical temperature of the system, i.e., the order-disorder transition temperature T_{OD} of the corresponding Ising model without field. For a square-lattice first-neighbor Ising-like system, exactly resolved, the condition is $\Delta/r\leqslant 2.27J$. For a one-dimensional short-range interaction system the order-disorder transition is located at 0 K; therefore no thermal first-order transition is expected for the one-dimensional (1D) Ising-like systems. Nonetheless the latter is a general property of one-dimensional systems with short-range interactions.

III. DYNAMICAL ASPECTS OF KINETIC ISING MODELS

The metastable state dynamics of the classical Ising system (temperature-independent field) has been widely studied by dynamic Monte Carlo, [21,20,22,11,30] or by classical [6,21] or field-theoretical droplet theories [9]. We outline here the main results of the nucleation theory in short-range interaction systems; the involved assumptions are discussed in detail in Ref. [4].

Both classical and field theoretical theories are based on the picture of the nucleation of the stable phase up to a ''critical droplet'' after which the growth proceeds without cost in energy. At a coarse-grained level, the system is described by a set of variables ψ_i and next, dynamic equations are established for the distribution functional $\rho(\{\psi_i\},t)$ as continuity equations in the form of the Focker-Planck equation:

$$\frac{\partial\rho}{\partial t}=-\sum_{i=1}^{N}\frac{\partial J_i}{\partial\psi_i}, \tag{3.1a}$$

with J, the probability density current, given by

$$J_i=-\sum_{j=1}^{N}M_{i,j}\left(\frac{\partial F}{\partial\psi_j}\rho+k_BT\frac{\partial\rho}{\partial\psi_j}\right). \tag{3.1b}$$

The underlying idea is that during nucleation, the metastable quasiequilibrium states lie in the vicinity of configurations which minimize the equilibrium free energy. Then, the relaxation from the metastable state occurs when the system moves from a local minimum of $\mathbf{F}\{\psi\}$ to another, passing nearby the lowest accessible saddle point of $\mathbf{F}$.

The steady-state solution of Eq. (3.1a) provides a constant nucleation rate $\mathbf{I}$, i.e., the inverse lifetime of the metastable state. The solution is obtained as follows: (i) the calculations are restricted to the vicinity of the saddle point; (ii) appropriate boundary conditions are imposed assuming that the stationary distribution function coincides with the equilibrium solution on the metastable side and is zero on the stable side (the latter condition means that droplets bigger than the critical size are removed from the system); and (iii) an expansion of $\overline{F}\{\psi\}$ is taken around the saddle point $\overline{\psi}$. The stationary current $\mathbf{J}$ is then derived from Eq. (3.1b), while the nucleation rate is obtained by integrating the current $\mathbf{J}$ through the surface in the vicinity of the saddle point. By noting respectively $\psi_+(r)$, and $\psi_-(r)$ the metastable and stable states and $\overline{\psi}(r)$ the saddle point state, the resulting nucleation rate can be written as

$$I = I_0 \exp(-\Delta F/kT), \tag{3.2}$$

where

$$\Delta F = F\{\overline{\psi}\} - F\{\psi_-\}. \tag{3.3}$$

For sufficiently small fields H, the saddle point solution $\overline{\psi}$ leads to the expression of $\Delta\overline{F}(R)$ for a d-dimensional droplet of the stable phase in the metastable medium:

$$\Delta\overline{F}(R) = \Omega_d^{(d-1)/d} R^{d-1}\sigma - |H|\Delta\psi\Omega_d R^d, \tag{3.4}$$

where $\Omega_d^{(d-1)/d}R^{d-1}$ and $\Omega_d R^d$, respectively, are the surface and the volume of the droplet, σ the surface energy at equilibrium and $\Delta\psi = \psi_+ - \psi_-$. Maximizing this expression with respect R yields the critical radius

$$R_c = \frac{(d-1)\sigma}{|H|\Delta\psi} \tag{3.5}$$

and the corresponding free-energy barrier is

$$\Delta F_c = \left(\frac{d-1}{|H|\Delta\psi}\right)^{d-1}(\Omega\sigma^d). \tag{3.6}$$

For kinetic Ising models (Glauber, Metropolis),

$$\Delta\psi = \Delta m = m_{\rm eq} - m_{\rm ms} \tag{3.7}$$

where $m_{\rm eq}$ and $m_{\rm ms}$ are the mean values of the one dimension order parameter (the magnetization) respectively at equilibrium and in the metastable state. The prefactor I_0 of the nucleation rate Eq. (3.2) can be written as in [31]: $I_0 = A(T)|H|^{b+c}$. Here $A(T)$ is a nonuniversal function depending only on the temperature and on the dynamic model, c is a purely dynamic constant, and b is an universal constant

$$b = \begin{cases} (3-d)d/2 & \text{for } 1<d<5,\ d\neq 1 \\ -7/3 & \text{for } d=3. \end{cases} \tag{3.8}$$

While, in general, the saddle-point calculations are based on approximate free-energy functionals given by Ginzburg-Landau or renormalization-group theory, for the two-dimensional Ising model one may obtain very accurate calculations thanks to the exact equilibrium Onsager's solution.

Concretely, as indicated by various works both analytical [31,32] and numerical [33], the free-energy cost of the critical droplet can be very well approximated by zero-field equilibrium quantities: (i) Δm is substituted by its zero field value, i.e., $\Delta m = 2m_{\rm eq}(h=0)$ given by the Onsager solution [34,35]; (ii) the surface energy σ is obtained by combining the Wulff construction of the droplet surface shape with the anisotropic zero-field surface tension [36].

An important feature of these results on the nucleation rate for short-range models is that the exponential term is independent of the system size. This means that the lifetime *does not diverge* for macroscopic sizes.

IV. MEAN-FIELD-LIKE MESOSCOPIC DYNAMIC: A DISCRETE MARKOVIAN DYNAMIC

In the previous section we outlined that nucleation theory is valid for small fields. Also, except for equilibrium soluble models, the theory requires the use of some phenomenological mean-field free energy functional, which is not valid near the critical temperature. Moreover, for more complicated systems, a correct free-energy functional would not be obvious to obtain, especially for disordered or diluted systems where it is difficult to account analytically for the spatial distributions. Also, the continuous field theoretical approach is not valid at low temperatures where the discreteness of the lattice becomes important.

We make use here of the method introduced by Lee *et al.* [12] (see also [18]). As shown in Ref. [12] it applies to weak and moderate fields, at any temperature [18,37].

A. Master equations and projection operator method

The static version of the Ising model does not itself contain any internal dynamics; the Hamiltonian commutes with the spin operators and therefore cannot provide any mechanism for the dynamics. The underlying dynamics of a system of spins comes for example from spin-phonon interactions and these could be introduced in the Ising Hamiltonian by the addition of corresponding quantum mechanical operators [10]. In this case the Hamiltonian would contain its own dynamics, and the evolution in time would be exactly provided by the Liouville equation for the microscopic density matrix ρ of the system. This is a highly complicated set of equations and it is needed to simplify it in terms of a few relevant mesoscopic or macroscopic variables. It is, however, very difficult to obtain explicit equations for cooperative systems, from this first-principle approach. Zwanzig and Nakajima [13,14,38] have introduced and developed a *projection operator method* in order to provide exact, non-Markovian equations for the distribution functions of the relevant observables. [The stochastic description of the dynamics is always associated with an important reduction in the number of the system's degrees of freedom and, if, initially, the (deterministic) equations of motion are ''Markovian,'' the rigorous reduced description must contain memory effects, in order to restore the lost information from the missing degrees of freedom.] In most cases, these exact (but formal) projections cannot be put in an explicit equation form. They are useful as a structure upon which we can impose approximations leading to Markovian microscopic equations; also, they may serve to know what has been left out and how to put it back in.

For some particular systems, it is possible to establish explicitly the Markovian master equation for the relevant variables, by introducing various approximations at the level of Zwanzig equation [39]. But generally this remains very difficult, and the master or Focker-Planck equations are introduced phenomenologically

$$\frac{\partial P_i}{\partial t} = -\sum_{i=1}^{N} P_i W_{i\to j} - P_j W_{j\to i}. \tag{4.1}$$

The dynamics is introduced only at the stochastic level, through the transition probabilities **W** as an artificial substi-

tute of the real underlying dynamics. Often, there are probabilities through an arbitrary choice from the detailed balance, which they must satisfy at equilibrium [40]:

$$P_i^{\mathrm{eq}} W_{i\to j} = P_j^{\mathrm{eq}} W_{j\to i}. \tag{4.2}$$

Despite its drastic reduction with respect to the initial Liouville equation, the phenomenological master equation [Eq. (4.1)] cannot be handled for a system of interacting spins: it represents a system of 2^N equations for an Ising model of N spins. The only rigorous way to solve it, except for particular cases [41], is provided by Monte Carlo methods. However this corresponds to an integration in time and becomes totally unsuitable for long-lived metastable states. It is, therefore, tempting to apply projection operator techniques at this level too, in order to reduce the dimensionality of the master equation. The benefit of such a reduction is easier to see in the discrete time version of the master equation:

$$\rho_i(t_2) = \sum_{j=1}^{N} W_{ij}\rho_j(t_1) \tag{4.3}$$

or in the vectorial notation

$$\vec{\rho}(t+1) = \mathcal{W}\vec{\rho}(t), \tag{4.4}$$

where $\mathcal{W}$, the stochastic matrix, is a $2^N \times 2^N$ matrix for an N-spin Ising system. Lee *et al.* [12] have adapted the standard projecting approach at the level of a microscopic Markov process described by Eq. (4.4). That is, for a macroscopic variable as the total magnetization **m**, the projected exact equation onto the subspace spanned by **m** is

$$\mathcal{P}\vec{\rho}(t+1) = \vec{P}(t+1) = \mathcal{P}\mathcal{W}\vec{P}(t) + \mathcal{P}\mathcal{W}\sum_{l=1}^{t} [\mathcal{Q}\mathcal{W}]^l \vec{P}(t-l) + \mathcal{P}\mathcal{W}[\mathcal{Q}\mathcal{W}]^t \vec{\rho}(0). \tag{4.5}$$

[Note that $m = N\times$ the reduced magnetization used in Sec. II.] $\mathcal{P}$ makes a projection of the microscopic distribution $\vec{\rho}(t)$, from a 2^N-dimension space over a subspace of dimension $N+1$ (the number of discrete components of the magnetization m). $\mathcal{Q}$ is the operator which projects in the complementary subspace, i.e., $\mathcal{P}+\mathcal{Q}=\mathbf{1}$. This ''motion'' equation contains non-Markovian contributions, representing the memory of the values of variable n [n is the number of spin up given by: $n=(1+m)/2$] at earlier times, and information about the initial state of the other variables (second and third terms, respectively). Neglecting the non-Markovian contributions, at this level, would lead to a Markov process described by a $N\times N$ stochastic matrix that can be handled for finite systems.

B. The macroscopic master equation for the order parameter: how to solve it

In this section we give some technical details concerning the derivation of the lifetime distribution moments, deduced from the macroscopic master equation resulting from Eq. (4.5) after the Markovian approximation. That is,

$$\mathcal{P}\vec{\rho}(t+1) = \vec{P}(t+1) = \mathcal{P}\mathcal{W}\vec{P}(t). \tag{4.6}$$

Here the vector $\vec{P}(t)$ belong to a 2^N-dimension space but has only $N+1$ nonzero elements corresponding to the number of values of the remaining variable n. Thus Eq. (4.6) is an equation for the distribution $P(n,t)$ of the macroscopic variable n. The projection $\mathcal{P}\mathcal{W}$ of the microscopic stochastic matrix $\mathcal{W}$ onto the subspace spanned by the coordinates of the order parameter n reduces to an $(N+1)\times(N+1)$ matrix, as the nonzero elements $\mathcal{P}\mathcal{W}$ correspond to the $N+1$ coordinates of the order parameter n. This projection will be noted as **W**. We will not calculate here the matrix elements provided by the projection. Indeed, as the choice of the microscopic stochastic dynamics is arbitrary, it is made as well at the level of the macroscopic equation, once the Markov property is justified. A natural choice for the elements of **W** follows from the macroscopic detailed balance given by Eq. (4.2):

$$P^{\mathrm{eq}}(n_1) W(n_1\to n_2) = P^{\mathrm{eq}}(n_2) W(n_2\to n_1). \tag{4.7}$$

In order to keep the local dynamics, identical to microscopic dynamics, we take $n_2 = n_1 \pm 1$, i.e., we assign the rate zero to the transition between configurations differing by more than one spin state. Next, as for the rate transitions obeying Eq. (4.7): we take Metropolis-like transition rates, while the diagonal element is derived from the normalization of the transition probabilities:

$$W(n\to n+1) = \min\left\{0, \frac{P^{\mathrm{eq}}(n+1)}{P^{\mathrm{eq}}(n)}\right\}, \tag{4.8}$$

$$W(n\to n-1) = \min\left\{0, \frac{P^{\mathrm{eq}}(n-1)}{P^{\mathrm{eq}}(n)}\right\}, \tag{4.9}$$

$$W(n\to n) = 1 - W(n\to n+1) - W(n\to n-1). \tag{4.10}$$

Of course, manipulating the $(N+1)\times(N+1)$ stochastic matrix elements requires knowledge of macroscopic equilibrium probabilities $P^{\mathrm{eq}}(n)$ given by

$$P^{\mathrm{eq}}(n) = \sum_{\langle i,n\rangle} P_i^{\mathrm{eq}} = \sum_{\langle E,n\rangle} D(E,n)\exp -\beta E \tag{4.11}$$

where $\langle i,n\rangle$ ($\langle E,n\rangle$) denotes a sum over configurations i (energies E) at fixed n. $D(E,n)$ the density of states stands for the number of states at the energy E and ''magnetization'' n. Thanks to the recent developments in the Monte Carlo sampling of the free energy [12,18,19,42,37], the macroscopic canonical distributions (or the density of states) can be obtained for systems of more than 10^4 spins. We use here the entropic sampling, in an optimized version developed by one of us [42]: through a unique procedure it furnishes the density of states in a dimensionless parameter space, which is relevant for any value of the model parameter set.

In the dynamics defined by the upper stochastic matrix, the time evolution of the macroscopic probability distribution $\vec{P}(\tau) = \{P(0,\tau), P(1,\tau), \ldots, P(n,\tau), \ldots, P(N,\tau)\}$ is determined by the simple equation

$$\vec{P}(\tau_\alpha) = \mathbf{W}^{\tau_\alpha}\vec{P}(0), \tag{4.12}$$

which follows recurrently from Eq. (4.4) and by using of the stationarity of **W**, as it appears in Eqs. (4.8). This is an essential property of a stationary Markov process. Then the metastable lifetimes are calculated by the absorbing Markov chains technique [43,44] as in Ref. [12]. A boundary is defined for the metastable phase, which determines the transient metastable states. Therefore a submatrix **T** of **W** corresponding to them defines the dynamics during the metastable lifetime. We denote the probability of existing and the probability of being absorbed at time τ_α $\mathcal{P}_{\rm ex}(\tau_\alpha)$ and $\mathcal{P}_{\rm abs}(\tau_\alpha)$, respectively. They are related by the following equation:

$$\mathcal{P}_{\rm ex}(\tau_{\alpha-1})=\mathcal{P}_{\rm ex}(\tau_\alpha)+\mathcal{P}_{\rm abs}(\tau_\alpha), \tag{4.13}$$

while $\mathcal{P}_{\rm ex}(\tau_\alpha)$ is simply given by

$$\mathcal{P}_{\rm ex}(\tau_\alpha)=\sum_n P_n(\tau_\alpha). \tag{4.14}$$

$\mathcal{P}_{\rm abs}(\tau_\alpha)$ can be understood as $P_{ml}(\tau_\alpha)$; the metastable lifetime distribution is easily derived as

$$P_{\rm ml}(\tau_\alpha)=\mathcal{P}_{\rm abs}(\tau_\alpha)=\sum_n [(\mathbf{T}^{\tau_{\alpha-1}}-\mathbf{T}^{\tau_\alpha})\vec{P}(0)]_n. \tag{4.15}$$

In a further step, the moments of the metastable lifetime distribution are obtained as:

$$\langle\tau_k\rangle=\sum_n \sum_{\alpha=1}^{\infty} [(\tau_\alpha)^k(\mathbf{T}^{\tau_{\alpha-1}}-\mathbf{T}^{\tau_\alpha})\vec{P}(0)]_n. \tag{4.16}$$

Then, using the properties of power series, the moments are simply expressed in terms of the fundamental matrix $\mathbf{N}=(\mathbf{I}-\mathbf{T})^{-1}$. For example, the first and second moments are

$$\langle\tau\rangle=\sum_n [\mathbf{N}\vec{P}(0)]_n, \tag{4.17}$$

$$\langle\tau_2\rangle=\sum_n [(2\mathbf{N}^2-\mathbf{N})\vec{P}(0)]_n. \tag{4.18}$$

The calculation of the average metastable lifetime only implies a matrix inversion, irrespective of the order of magnitude of the lifetime.

C. One-variable and two-variable macroscopic dynamics

The question remains: what are the errors introduced by neglecting the non-Markovian contributions, when we only seek to obtain the metastable lifetime distribution? There are theoretical arguments [45,46] to convince that the memory effects may be neglected on a time scale much larger than the characteristic time of the eliminated, rapid variables. This means the variables, involved in the reduced equations should *slowly vary* with respect to those, which are eliminated by the projection technique. In the present work, the variables eliminated in the projected equation [see Eq. (4.5)] are the spin state of each site and, i.e., the complete spin configuration has been replaced by the total magnetization. However, in the metastable state, the spin configurations have changed several times during a time interval where the magnetization practically does not varies. In other terms, memory effects are lost at time intervals which are large with respect to the spin correlation times, but remain small with respect to the metastable lifetime. The calculations of Lee *et al.* [12] are highly convincing: they compared the dependences of the metastable lifetimes on the applied field, obtained either by the microscopic (Monte Carlo) dynamic, or by the projected macroscopic dynamic. They also give an excellent agreement at weak and moderate fields. For stronger fields, the metastable lifetime became shorter, i.e., it is not large enough with respect to correlation times.

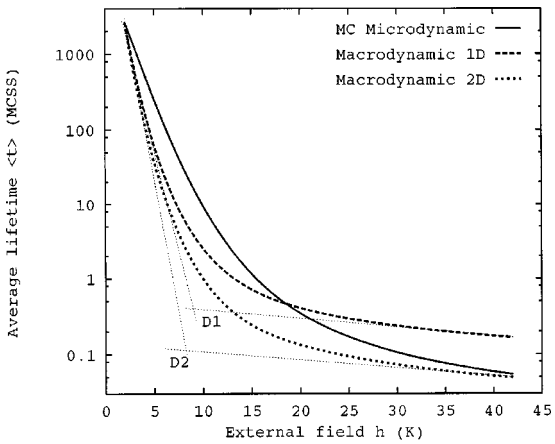

FIG. 2. The average lifetime of the metastable state (relaxation time from $m=-N$ to $m=0$) of the classical square lattice Ising model plotted as a function of the applied field, for a 24×24 lattice, at $T=0.88T_C$. We compare the results obtained by the microscopic Metropolis dynamic (full line) with those from the macroscopic dynamic approximation with one variable, m (crosses-dashed line) and two variables m and s (dotted line), with m,s=magnetization and energy, respectively. The field varies in the stochastic region. All values are calculated by averaging over 1000 independent paths. The time scales are rescaled at the lower field value and are expressed in Monte Carlo steps per spin (MCSS); the field is expressed in temperature units (i.e., energy). The straight lines approximate the stochastic (weak fields) and the deterministic (strong fields) regimes for both the one-variable and the two-variable dynamics; the points $D1$ and $D2$ correspond, schematically, to the crossover points (dynamical spinodal points) for the one- and two-variable dynamics, respectively.

We now consider the number of macroscopic variables in the reduced Markovian dynamic. It is expected that the larger the number, the closer the result to the true microscopic (N-variable) dynamic. Following our previous work [18] a two-variable dynamic is obtained by the projection onto a subspace spanned by total magnetization and total energy. Energy is also a slow variable for the metastable state relaxation. In Fig. 2 we compare the metastable lifetimes, obtained by the Monte Carlo microscopic dynamic, by the one-variable and the two-variable Markovian dynamic, calculated in function of the applied field. Technical details on the calculations are given in the next section. The calculations are made for a 24×24 square lattice, at $T=0.88Tc$. The three dynamics have different time scales but we rescaled them in such a way that the lifetimes coincide at the smallest field value, where the dynamics are quite equivalent. Surprisingly, the two-variable dynamic does not fit better the Monte Carlo curve than the one-variable dynamics.

From the point of view of the Markovian approximations, the differences in the time-scales between the three dynamics can be interpreted as due to the time coarse-graining which is implicitly involved in the Markovian approximation. The size of ''time grain'' depend on the physical details (correlation times); in this case it depends on the field value. This explains the deviations which are observed between the three lifetimes curves as the field is increased.

The paradoxical situation of a two-variable approximation which is not really improved with respect to the one-variable approximation, is not rare in statistical mechanics, e.g., it is also present in the Kikuchi cluster variational method (CVM) for the order-disorder transitions in solids [47,48]. It is an entropic approximation at equilibrium, which treats clusters of a cell in the mean-field approximation, but correctly includes all the spatial correlations between sites in the cluster. It is well known that increasing the cluster size does not lead always to an improvement of the approximation, as would be expected; it is specially the case for frustrated systems [49]. The explanation here should sought in terms of the additional correlations associated with the second macroscopic variable. [There are cases where including only a part of the correlations may be followed by a lack of the constraints serving as boundary conditions for the latter.] Also, although a macroscopic dynamic based upon the magnetization and energy conserves an important part of the microscopic information, there is an essential quantity in nucleation phenomena which we miss here, that is the droplet size. We think that a macroscopic dynamic including the droplet size would be very close to the microscopic one.

For relatively strong fields ($H \gtrsim 25\,\mathrm{K}$, for the sizes considered here), the one-variable dynamic approximation is clearly less appropriate than the two-variable case because, as it has been argued in Ref. [18], they have different ''mean-field-like'' spinodals, i.e., the field values at which the ''saddle point'' vanishes are different. This leads to the collapse of the barrier in one dimension prior to the collapse of the barrier in two or more dimension distributions. However, for these fields, the metastable lifetimes are short and the above arguments have little practical impact, all the more so that the Markovian approximation is less valid at these fields. We will use therefore the macroscopic one-variable Markovian dynamic to the Ising-like model with a temperature dependent field, as it involves much smaller matrices.

V. THE ISING-LIKE MODEL IN THE ONE-VARIABLE DYNAMIC

We apply here the one-variable mesoscopic approach to the calculation of the metastable lifetimes for the two-dimensional (2D) Ising-like model, expressed with a temperature-dependent effective field. We consider only the nearest-neighbor (NN) ferromagnetic interactions. We use the dynamic defined in the previous section, with the matrix coefficients given in terms of macroscopic canonical distributions; they are calculated semi-numerically, for each system size, through the density of states $D(M,E)$, which is sampled by Monte Carlo entropic sampling. As our density of states ($D[M,S]=D[M,E(M,S)]$) is a function of dimensionless variables $S=\Sigma_{\langle i,j\rangle}s_i s_j$ and $M=\Sigma_i s_i$,—so as $E=h_{\mathrm{eff}}M-JS$—(see Ref. [18]), there is a considerable advantage that the sampling be performed only once for a system size, allowing for a continuous variation of the model parameters: coupling constant J, energy gap for the two spin states Δ, degeneracy ratio g and, of course, temperature T [18].

The initial state distribution is taken in a particular metastable configuration, where all the spins are opposite to the effective field. Due to the temperature dependence of the field, for $T<T_{\mathrm{eq}}$ the metastable state is $m=+1$ and, for $T>T_{\mathrm{eq}}$ $m=-1$. The transient metastable states are chosen between all configurations corresponding to the same sign of the order parameter, i.e., $-1\leqslant m<0$ for $T>T_{\mathrm{eq}}$ and $0<m\leqslant 1$ for $T<T_{\mathrm{eq}}$. This defines the absorbing boundary for the metastable state at $m=0$. It is well known for short-ranged interaction models [1,50,2] that there is no unique way to define the metastable region of the configuration space, i.e., the metastable lifetimes will finally depend on the arbitrary location of the boundary. However, as it was shown in different studies concerning the Ising model in Monte Carlo dynamics [22,11], the results are not really sensitive to the location of the boundary, as long as the boundary is far from the metastable quasiequilibrium m value. Therefore the absorbing boundary is fixed here at the simple value $m=0$. Also, we always initialize the metastable state in a saturated state; indeed we have checked that the results did not depend on the initial distributions in the metastable region.

The average value $\langle\tau\rangle$ of the lifetime (i.e., first-passage time), calculated as described in Sec. IV B, has been divided by the number of spins L^2 in order to give the times in units of Monte Carlo step by spin (MCSS). It corresponds to the dynamical assumptions that each spin interacts with the heat bath independently of the other spins, and that the magnitude of the fluctuation energy per spin, transmitted by the heat bath, only depends on temperature but not on the system size (the approximation of an ''infinite'' heat bath).

We shall first investigate the specific role of temperature for the dynamic of this model. Next we analyze the results on the lifetime in relation with the behavior of spin-crossover systems [26], for different values of coupling constant J ($60\,\mathrm{K}\leqslant J\leqslant 150\,\mathrm{K}$) and energy gap (crystal field) Δ. ($200\,\mathrm{K}\leqslant\Delta\leqslant 1000\,\mathrm{K}$). All the calculations were performed in the 2D NN Ising-like model, for the system sizes 16×16, 24×24, and 32×32 spins.

A. The ambiguous role of temperature

In Fig. 3(a) we show the lifetime of the metastable states on each side of the thermal first-order transition ($T\leqslant T_{\mathrm{eq}}$: $m=+1$; $T\geqslant T_{\mathrm{eq}}$: $m=-1$), as a function of temperature. The peak in the lifetime corresponds to the first-order transition at $T_{\mathrm{eq}}=(\Delta/\ln r)$.

A striking property displayed by Fig. 3 is the net asymmetry in the metastable lifetimes for the high temperatures and low temperatures. While the high-temperature metastable state vanishes rapidly as temperature is increased above the transition temperature T_{eq}, the low-temperature metastable lifetime decreases less rapidly when temperature is decreased below T_{eq}, goes to a minimum, and finally increases at low temperatures. Obviously the temperature plays a double role here: it is both the driving force of the equilibrium phase transition through the variation of the effective

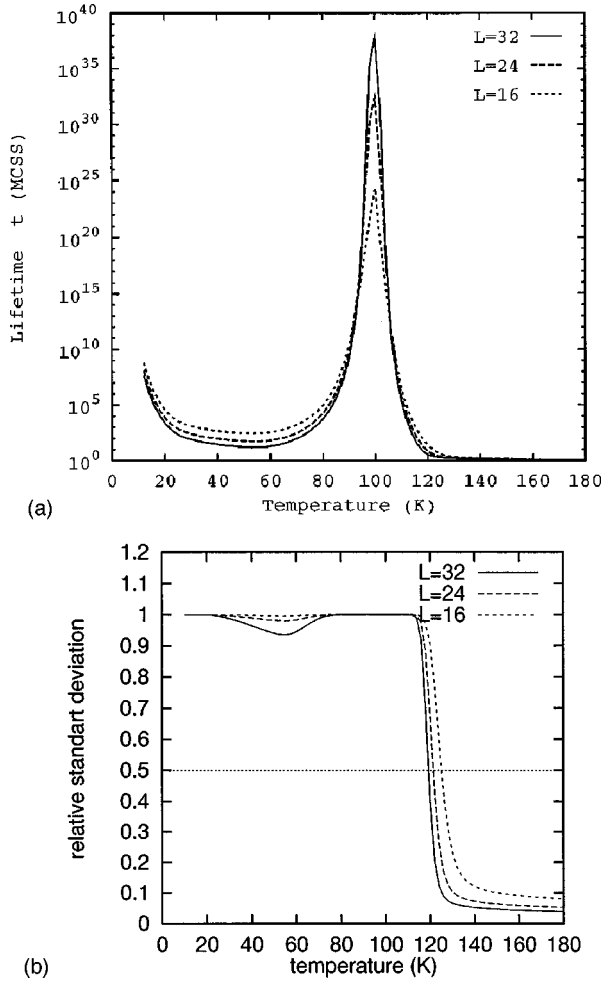

FIG. 3. The metastable lifetime for a 2D Ising-like model as a function of temperature with $J=100$ K, $\Delta=500$ K, $g=150$ and size $L\times L$, with $L=16,24,32$. The timescale is converted in Monte Carlo steps per spin (see text): (a) average lifetimes (first moment of the lifetime distribution); (b) relative standard deviation (second moment of the lifetimes distribution).

field and it is also the source of the thermal fluctuations energy, which induces the crossing of the energy barrier. Above $T_{\rm eq}$, the two driving forces change in the same way. Below $T_{\rm eq}$ the two driving forces of the relaxation change in opposite ways: the destabilizing effective field increases while the fluctuation energy decreases. The minimum at low temperatures occurs because at these temperatures the fluctuation energy k_BT decreases more rapidly than does the energy barrier.

B. The identifications of different regimes

In the following, our interpretation will be partially helped by the known results from the simple Ising system under an external field. First, at weak effective fields the lifetime increases with the number of spins, just as at zero field. The crossover effective field, the thermodynamical spinodal point (THSP) [11] depends on the temperature and the corresponding crossovers for the present model when one varies the temperature (the effective field and the temperature vary simultaneously), the two temperatures $T^{-}_{\rm THSP}$ and $T^{+}_{\rm THSP}$ obeying

$$|\Delta - T\ln r| = \frac{1}{L}\left[\frac{\Xi T}{2m_{\rm eq}T_{\rm THSP}}\right]^{1/2}. \tag{5.1}$$

As in Ref. [11], this is established by considering the limit temperature for which the critical droplet occupies the whole system. In these temperature (effective field) regions, the lifetime increases exponentially with the system size, as for stable equilibrium states. As $m_{\rm eq}(T)$ varies very slowly around our transition temperature $T=0.44T_c$ [35], while $\Xi(T)$ (the surface tension of the nucleating droplet) being a decreasing function of temperature (see Ref. [51]) then, the ''thermodynamic spinodal'' temperature will rapidly converge to the transition temperature T_t when the size of the system increases. Next, for larger temperature differences $|T-T_t|$ (the effective unfavorable field for the metastable state increases) the Ising system is in the ''stochastic'' region, according to the definitions given in Ref. [22] for the standard Ising system. It follows from Fig. 3(a) that the lifetimes are decreasing functions of the size in a large range of temperatures. In this temperature (field) region, according to droplet theory, the lifetime should be inversely proportional to the size, as given by (see Ref. [11]):

$$\langle\tau\rangle = [A(T)]^{-1}N^{-1}H^{-1}\exp\left(\frac{\Delta F}{k_BT}\right), \tag{5.2}$$

where $\Delta F=(\Xi(T)/|H|)$. Therefore, the behavior is somewhat different for the present Ising-like system, because of the temperature dependence of the prefactor $A(T)$ and of $\Delta F(T)$, but the variation with size is the same.

In the stochastic region of the field (here the temperature) the growth of the stable phase occurs through only one droplet (very small probability for other droplets to appear for these fields) and the life times are very large. Hence, it is a Poisson process a macroscopic characteristic of which is that the standard deviation of the lifetime distribution is of the same order as its first moment. For larger fields (i.e., larger $|T-T_t|$ here) the growth occurs via several droplets, the standard deviation of $\langle\tau\rangle$ is much smaller than $\langle\tau\rangle$ and the latter is given by

$$\tau(h,T)\approx|h|^{-\,b+c+d/d+1}\times\exp\left[\frac{\beta\Xi(T)}{(d+1)|h|^{d-1}}\right]. \tag{5.3}$$

As follows from Sec. III (see also Refs. [9, 31] and [22,11]), $b+c=3$ in two dimensions and, then we have for the average lifetime of the square lattice Ising-like model:

$$\tau(h,T)\approx|\Delta-rT|^{-\,5/3}\exp\left[\frac{\beta\Xi(T)}{3|\Delta-rT|}\right]. \tag{5.4}$$

The crossover field between the two regimes, as discussed in Ref. [11], is determined by considering the field for which the distance between droplets is equal to the critical droplet size; this field was called the dynamical spinodal point (DSP) in Ref. [22] and is given by

$$|h_{\rm DSP}|\simeq\frac{\beta\Xi(T)}{3\ln L}. \tag{5.5}$$

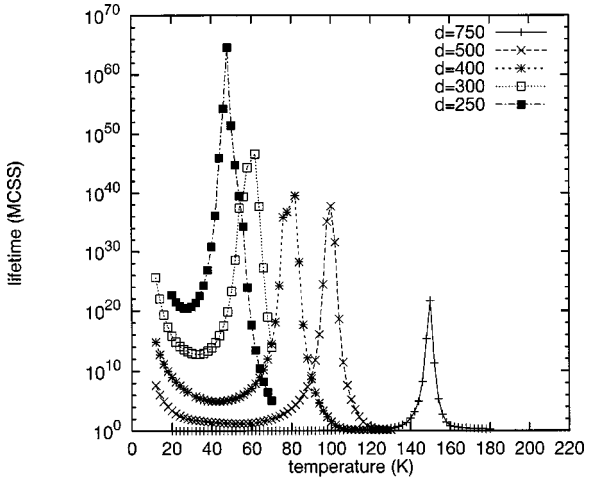

FIG. 4. The average lifetime of the two metastable states as a function of the temperature for the 32×32 system, for $J=0.44T_C$, $g=150$ and for different values of the separation field Δ from 250 K (full squares) to 750 K (crosses).

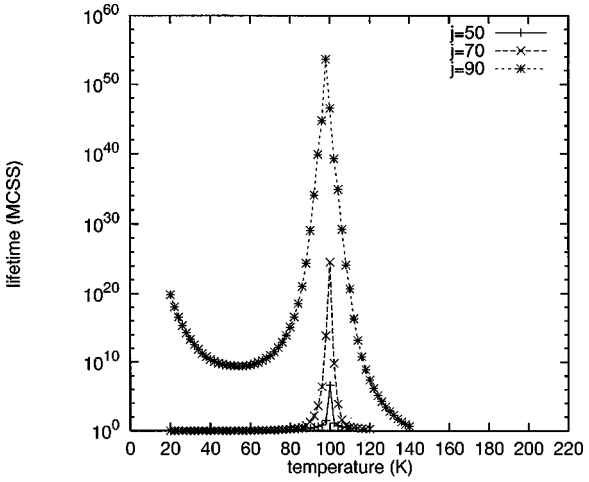

FIG. 5. The average lifetime of the two metastable states as a function of temperature for the 32×32 system at different values of the coupling constant J. $\Delta=500$ K, $g=150$ and $J=50$ K, 70 K and 90 K.

The corresponding spinodal for the temperature in the Ising-like model remains as

$$|\Delta - rT_{\mathrm{DSP}}| \simeq \frac{\beta \Xi(T_{\mathrm{DSP}})}{3 \ln L}. \tag{5.6}$$

It follows from Eqs. (5.6) that the DSP in temperature, as a solution of Eq. (5.6), does not have a monotonic behavior with the temperature (in contrast with the standard Ising case). Indeed, the H_{DSP} is a decreasing function of temperature, which indicates a complex behavior of the dynamic spinodal temperature (DST), for the high-spin metastable state.

As an illustration, we have calculated the standard deviation by the macroscopic dynamics method, which is shown in Fig. 3(b). As argued in Ref. [22], the relative standard deviation σ_r of $\langle\tau\rangle$ is of the order of $\langle\tau\rangle$ in the stochastic zone and the crossover regime from stochastic to deterministic is observed as soon as σ_r is less than 1. In Fig. 3(b) the crossover appears twice: at high temperatures, and around the minimum of the lifetime at low temperatures, while around the first order transition and at low temperatures the relaxation of the metastable state is entirely a stochastic processes. As it appears in both Fig. 3(b) and Eq. (5.6) the dynamical spinodal temperature is size dependent.

C. On the spin-crossover systems

In Fig. 4, the temperature dependence of the lifetime is shown for different values of the ratio Δ/r. The variation of Δ in spin-crossover compounds can be physically realized by applying an external pressure (see Ref. [26]). Δ and T_{eq} are increasing functions of pressure because the low-spin state has a smaller volume.

The effect of J is shown in Fig. 5. As is illustrated in Figs. 4 and 5, the lifetime minimum of the low-temperature metastable state disappears for strong gap Δ or weak coupling constant J. In fact the relevant quantity to be considered is the ratio J/T_{eq} because of the competition between the monotonic decrease of the effective field $d_{\mathrm{eff}}=\Delta-rT$ with temperature and the strong reduction of the fluctuations (with energy k_BT) at low temperatures. Indeed, qualitatively, we can just observe that there is no longer a minimum in the lifetime, if the energy barrier vanishes before the fluctuations begin to decrease faster. This can occur either for weak coupling constant J (weak, rapidly vanishing barrier) or for high first-order transition temperatures. In this case, the effective field d_{eff} is located in the *strong field* region [11], which corresponds here to low temperatures [52].

Next, it follows from Figs. 4 and 5 that the lifetime of the low-temperature metastable state may be very important, even far from the first-order transition region; especially if the transition is located at low temperatures, as happens for a relatively weak energy gap Δ. For estimating the orders of magnitude expected in spin-transition systems, it should be noted that the typical spin state relaxation rates in these systems [53] are between 10^6 and $10^9\ \mathrm{s}^{-1}$ at high temperatures. This can be considered as typical spin-flip frequency. It turns out that, while Δ varies from 300 to 250 K, the lifetime minimum of the low-temperature (high-spin) metastable state varies from a few hours to millions of years for the sizes considered here. This means that the low spin state would hardly (or never) be observed for, relatively, weak values of the energy gap Δ (200–300 K) or strong values of the interaction parameter J, in systems of the size considered here ($\sim$300 up to 1024 spins).

The cooperative effects investigated here seem able to increase the lifetime of the metastable high-spin (low-temperature) state by up to a factor $\sim$10 orders of magnitude, compared to the intrinsic lifetime, i.e., the inverse of the intrinsic spin-flip frequency.

Of course the present results correspond to a first step in the study of spin-transition systems. A more realistic approach should include some additional considerations about the nature of spin-transition molecules and their interactions. We will mention here two of them.

(i) There is experimental evidence [26] for an intramolecular energy barrier between both spin states. As a possible extension of the model, this energy barrier might be accounted for explicitly and should lead to an Arrhenius-type

thermal dependence for the individual spin-flip frequencies. Such an easy extension would result in increasing the lifetimes for both spin states, especially at low temperatures, as suggested by the experiments. However the height of the energy barrier should be specific of each type of molecular unit.

(ii) From other viewpoints concerning the nature of the interactions in spin transition systems [26], a realistic model should contain both short- and long-range interactions. As a consequence, the lifetimes would strongly increase. Also, the size dependence of the lifetime time is very different between short and long range interactions. While for the former, the lifetime, after being inversely proportional with the size, becomes size independent at larger sizes (all other parameters kept constant) [11], for the later the lifetime exponentially increases with the size. It suggests that experiments on the relaxation time on small systems might bring new elements about the nature of interactions in spin-transition systems and about their applications for information storage, strongly related with the stability of the phases. In addition, we think that it would be interesting to extend this kind of study to a similar photoexcitable system under permanent light irradiation.

VI. A POSSIBLE FINITE-SIZE SCALING

Some qualitative arguments may be developed allowing to speculate for the large size behavior, using the results from smaller sizes. An essential point is the difference between the one droplet and the multidroplet growth of the stable phase. In the former the lifetime is inversely proportional to the size while in the latter it is size independent. Consequently, the size scaling will not consist of a monotonic extrapolation, but will involve a crossover between the regimes, for a temperature-dependent size value (the dynamical spinodal size), as it appears in Eq. (5.6). Conversely, at a given size, different temperatures will correspond to different regimes: while the multidroplet nucleation regime is reached far from the first-order transition temperature, the points closer to the transition point have important lifetimes and are still in the single droplet regimes. As an illustration, in Fig. 6 we show the relative standard deviation for $L=16$ and $L=32$.

It suggests that for larger sizes, the lifetime will be the same around the lifetime's minimum region of the temperature, while it will be lower in the region closer to the transition, where they are very important for the sizes considered here. In other words, we can be sure to have reached the asymptotic behavior at the points where the relative standard deviation is lower than 0.5. An empirical finite size-scaling may, then, be developed simply by extrapolating the laws for the lifetimes at the two regimes, together with the law for the dynamical spinodal temperatures, using the small size results. However, a confident finite-size scaling requires reaching sizes far beyond the dynamical spinodal size, and will be the object of another work. We think that these simple qualitative arguments can apply to other short or medium-ranged models as long as the concepts of the droplet nucleation theory are valid.

VII. DISCUSSION AND PERSPECTIVES

We firstly point out a major advantage of the present method for studying the relaxation of metastable states in

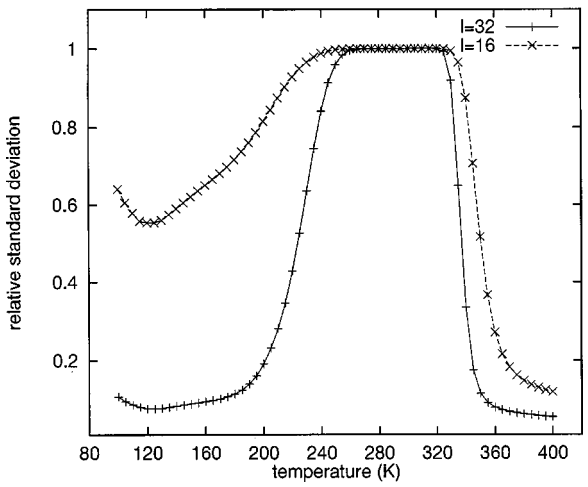

FIG. 6. Relative standard deviation of the average metastable lifetime for the 32×32 (lower curve) and the 16×16 (upper curve) systems; $J=250$ K, $\Delta=1500$ K, and $g=150$. A relative standard deviation close to one is typical of the single-droplet regime.

temperature driven, first-order transitions. The method starts from a sampled density of states which is used for calculating macroscopic probabilities at any temperature, in order to establish a macroscopic dynamics that can be solved semi-analytically. Concretely, the important numerical effort—for obtaining the density of states—has to be made only once; then the resolution of the dynamics only involves algebraic manipulations of matrices, irrespective of the dynamic characteristics. Obviously, the amount of information included in the density of states is huge and, indeed, requires much more CPU time than multicanonical sampling [16], which provides the free energy (i.e., equilibrium distribution) at a given temperature. However, the multicanonical sampling has to be made for each temperature, so as the entropic sampling appears as the most suitable method for temperature-dependent problems and, more generally, for all investigations where several parameters have to be explored. The advantage is even greater, since we have proposed a version of the entropic sampling iterative procedure, which can save an important amount of CPU time, making it possible to work with systems larger than 1000 sites [37]. Also, we believe that further improvements of the entropic sampling iterative procedure are possible, specially by using more fundamental mathematical tools.

The validity of the method, especially its accuracy for strong metastable states [12]—weak field, low temperature—is related to the specificity of the metastable states relaxation, which can be represented as very slow, *quasiequilibrium* processes. From this point of view, the droplet theory of Langer, based upon similar hypothesis about the nature of the relaxation is not less valid for strong metastable states. Nevertheless, we stress that the essential advantage of this method in studying metastable states (slow relaxations), is that it can be used, in principle, for any model. The method is obviously limited by the cost of the procedure, but the cost is only related with the number of macroscopic variables spanning the expression of energy's eigenvalues. Also, we think the method is especially suited for side-disorder systems, where the spatial distribution of the vacancies (impurities) is hardly accounted for analyti-

cally, while the sampling procedure works the same as in the pure system.

At a more fundamental level, we think the present method can offer a supplementary tool for theoretical studies on nonequilibrium statistical physics and metastable states. Indeed, assuming the Markov property for the macroscopic variables is equivalent to neglecting the influence of a part of the microscopic information relevant to the evolution of the macroscopic variables. An interesting challenge should be the gain of a deeper insight into the nature and the validity of the Markovian approximation in the dynamics of the metastable states. Concretely, the validity of the Markov approximation is related to the characteristic time scales in microscopic and macroscopic dynamics with respect to the metastable lifetime. The access to the time scales should involve the calculations of time correlation functions in microscopic and 1D and 2D macroscopic dynamics; their comparison might explain the behaviors of the lifetime variation (with the field or temperature) in the three dynamics. This encounters fundamental problems of statistical physics as are the *time coarse-graining* of the information, the role of the entropy creation in the slow dynamics of systems far from equilibrium, or the quantitative criterias based upon correlation functions for the distinction between equilibrium and nonequilibrium states.

In conclusion, we think that the present method is very well suited for the study of metastable states and the calculation of their lifetimes around temperature-driven first-order transitions. It should be preferred to other methods, especially for studying small systems like nanoparticles and, better, diluted systems. For large size systems, the density of states calculation—on which is based the method—is, at the present, very expensive, but a phenomenological finite-size scaling might be established.

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[39] It is the case, for the above Ising system with spin-phonon coupling in the limit of equivalent neighbors interactions

($\forall\{i,j\} J_{ij}=J$: ''mean-field'' model) [10,54], for a system of harmonic oscillators coupled in a bilinear way with a ''heat bath'' of linear oscillators [55] or, in general, for a pair-interaction potential in the limit of weak interaction parameter [13].

[40] There is a way for justifying such an ''artificial'' choice just by stressing that the transition probabilities out of equilibrium would be the same as at equilibrium, as long as they account for the same underlying physics. Nevertheless, not all the information from the system is included in these transition probabilities for the spin configurations, and what has been left out perhaps would not have the same incidences in all the situations.

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