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Relaxation Mode Analysis of Nonlinear Birth and Death Processes[1]

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Nonlinear birth and death processes with one variable are considered. The general master equations describing these processes are analyzed in terms of their eigenmodes and eigenvalues using the method of a WKB approximation. Formulas for the density of eigenstates are obtained. The lower lying eigenmodes are calculated to investigate long-time relaxation, such as relaxations of metastable and unstable states. Anomalous accumulation of the lower lying eigenvalues is shown to exist when the system is infinitesimally close to a critical or marginal state. The general results obtained are applied to some instructive examples, such as the kinetic Weiss–Ising model and a stochastic model of nonlinear chemical reactions.

KEY WORDS: Nonlinear birth and death process; WKB approximation; relaxation time of metastable states; relaxation time of unstable states; kinetic Weiss–Ising model; stochastic model of chemical reactions.

1. INTRODUCTION

Relaxation phenomena in a large system have been recognized to be important in many branches of science. The basic method to understand those phenomena is the consideration of deterministic differential equations (DDE) such as macroscopic transport laws or kinetic laws in which fluctuations are neglected. In a nonlinear system the DDE is nonlinear and may have multiple stationary states under certain conditions.[3] In this approach, when an initial state is one of the stationary states the system stays at that state forever even if the state is asymptotically unstable or metastable. Those unphysical results are, of course, caused by the neglect of fluctuations.

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In order to take fluctuations into consideration, a stochastic approach has to be envisaged. There are two different stochastic approaches, the Langevin method and the approach using a birth and death process. The former has no clear physical justification except in simple cases such as linear ones or near equilibrium. The latter is more transparent and satisfactory, and therefore we will consider birth and death processes from now on.

In a previous paper[1] we developed a general approximate theory for relaxation and fluctuation phenomena of macrovariables. In this theory, propagation of the extensive property of the nonequilibrium probability distribution plays an essential role and the method of the system-size expansion[2] becomes powerful. Time-dependent behavior of the mean values and the fluctuations of macrovariables can be calculated with the evolution equations.[4] The evolution equation of the mean values is given by the DDE and has a stationary solution at each extremum of a free-energy-like function calculated by the equilibrium distribution. It has been shown by Suzuki that the extensive property of the nonequilibrium distribution propagates only within a time interval of $O(\Omega^0)$, where Ω is the size of the system.[5] Therefore, the short-time behavior is almost completely described by the theory. It is a crucial point of the theory developed by Kubo *et al.*[1] that ordering of the magnitudes of the system size and the time scale is fixed. The same difficulty appears in the deterministic theory. In the case where the initial state is asymptotically unstable the instability of the system appears as the divergence of the variance of the fluctuations. However, the relaxation of the metastable state cannot be treated within our previous theory.[1]

We will restrict our attention in this paper to nonlinear stationary birth and death processes with one variable. A master equation describing such a process is a differential-difference (or difference) equation in continuous (or discrete) time. A few simple models can be solved analytically.[3] In most models the master equation is formally expressed by a Kramers–Moyal expansion and approximated by a Fokker–Planck equation. These approximation procedures are in general invalid, especially in far-from-equilibrium situations, as was shown in the previous paper.[1] In this paper the master equation is analyzed as a differential-difference equation by a method for treating large perturbations developed by Bethe a number of years ago.[7] This method is equivalent to a WKB approximation for difference equations. In order to apply the method to birth and death processes, we will assume that the transition probabilities obey detailed balance.

Most eigenmodes have large eigenvalues of $O(\Omega)$, which contribute to a short-time relaxation. We will analyze in some detail the lower-lying

[3] For example, the Ehrenfest model and the Alkemade diode model are solved analytically. Some quantum models are treated in Ref. 6.

eigenmodes, i.e., the eigenmodes of the lower eigenvalues, since they are important in long-time relaxation such as the relaxation of unstable and metastable states. The order of accumulation of the lower-lying eigenvalues in the thermodynamic limit is considered in the case when the system is infinitesimally close to a critical or marginal point. Some of the results in this paper have already been presented in the previous one. However, they are shown again to make the present paper self-consistent.

After introducing the master equation and discussing its properties in Section 2, we summarize the method for treating large perturbations in Section 3. We then apply this method to the master equation and obtain the eigenmodes and the eigenvalues in Section 4. Relaxation times of unstable and metastable states are calculated in Section 5. In Section 6 the general results obtained in the previous sections are applied to some examples which have been discussed previously by a number of authors.

2. PRELIMINARIES

We assume that a macrovariable X is a discrete stochastic variable obeying a stationary birth and death process. Then, its probability distribution $P(X, t)$ satisfies a master equation of the form

$$(\partial/\partial t)P(X, t) = \sum_r W(X - r, r)P(X - r, t) - \sum_r W(X, r)P(X, t) \quad (1)$$

where $W(X, r)$ is a transition probability per unit time from X to $X + r$. It is assumed that each transition takes place in an infinitely short time interval, and that the transition probability can be normalized by a system size Ω,[4] i.e.,

$$W(X, r) = \Omega w(x, r) \quad (2)$$

where $x = X/\Omega$ is a normalized intensive macrovariable corresponding to X.

If a unique statistical equilibrium $P_e(X)$ exists for the process, the transition probabilities must be conditioned by it, i.e.,

$$\sum_r W(X, r)P_e(X) = \sum_r W(X - r, r)P_e(X - r) \quad (3)$$

We assume in this paper that the transition probabilities obey the stronger condition of detailed balance

$$W(X, r)P_e(X) = W(X + r, -r)P_e(X + r) \quad (4)$$

for each possible value of r.

[4] The assumption was made in Ref. 1. For chemical reactions a mathematical discussion is given by Kurtz.[8]

From the condition (4) we can write the transition probabilities in the form

$$W(X, r) = \overline{W}(X \mid X + r)P_e^{1/2}(X + r)P_e^{-1/2}(X)$$
$$= \overline{W}(X \mid X + r) \exp \tfrac{1}{2}[\Phi_e(X + r) - \Phi_e(X)] \tag{5}$$

where $\overline{W}$ is symmetric, i.e.,

$$\overline{W}(X \mid X + r) = \overline{W}(X + r \mid X) \tag{6}$$

and the equilibrium distribution can be expressed in terms of a free-energy-like function $\Phi_e(X)$ or $\phi_e(x)$ such that

$$P_e(X) = \text{const} \times \exp \Phi_e(X) = \text{const} \times \exp[\Omega\phi_e(X/\Omega)] \tag{7}$$

A nonequilibrium probability distribution $P(X, t)$ will be transformed with $P_e(X)$ into

$$\psi(X, t) = P_e^{-1/2}(X)P(X, t) \tag{8}$$

which gives a symmetrized master equation

$$(\partial/\partial t)\psi(X, t) = -\sum_r W(X, r)\psi(X, t) + \sum_r \overline{W}(X - r \mid X)\psi(X - r, t) \tag{9}$$

We will write Eq. (9) in a vector form

$$(\partial/\partial t)\boldsymbol{\psi}(t) = -\Gamma\boldsymbol{\psi}(t) \tag{10}$$

where

$$[\boldsymbol{\psi}(t)]_n = \psi(r_0 n, t) \tag{11}$$

and

$$\Gamma_{nm} = \begin{cases} \sum_k W(r_0 n, kr_0), & n = m \\ -\overline{W}(r_0 n \mid r_0 m), & n \neq m \end{cases} \tag{12}$$

where $r = r_0 n$ and r_0 denotes the smallest number of "units" that change in a one-step transition, i.e., number of spins or number of molecules. The transition matrix Γ does not depend on time since we have assumed the process to be stationary. An eigenvector $\boldsymbol{\psi}_j$ and its corresponding eigenvalue λ_j of Γ can be obtained by the eigenvalue equation

$$\Gamma\boldsymbol{\psi}_j = \lambda_j\boldsymbol{\psi}_j \tag{13}$$

From the definition of Γ it is clear that the lowest eigenvalue λ_0 is zero and the corresponding eigenvector $\boldsymbol{\psi}_0$ is given by

$$(\boldsymbol{\psi}_0)_n = P_e^{1/2}(r_0 n) \tag{14}$$

Using the eigenvectors ψ_j of Γ, we obtain the solution of Eq. (10) as

$$\psi(t) = \sum_j p_j e^{-\lambda_j t} \psi_j \tag{15}$$

where

$$p_j = (\psi_j, \psi(0)) \tag{16}$$

From Eq. (15) we can write the solution $P(X, t)$ as

$$P(X, t) = P_e(X) + \sum_{j>0} p_j e^{-\lambda_j t} P_e^{1/2}(X) \psi_j(X) \tag{17}$$

The transition matrix Γ can easily be shown to be a symmetric, semipositive definite form from its definition. All eigenvalues of Γ are therefore real and nonnegative,[9] and we can obtain the following general conclusion. If a master equation of a system is described by transition probabilities that obey a condition of detailed balance, there do not exist any circulation motions in the system.

3. A METHOD FOR LARGE PERTURBATIONS

The master equation (1) is obtained in the form of a differential-difference equation in the last section. It can be expressed by the Kramers–Moyal expansion, which is an infinite-order differential equation and where one assumes that the expansion converges. In this paper, the difference equation (13) will be directly analyzed by a method for large perturbations developed by Bethe in 1938.[7] The method is equivalent to a WKB approximation for difference equations. We summarize in this section the method presented in Bethe's classic paper with slight modifications in order to apply it to birth and death processes.

The matrix elements of Γ will be denoted by

$$\Gamma_{nn} = W(n) \tag{18}$$

$$\Gamma_{n,n-k} = \Gamma_{n+k,n} = -A_k(n + \tfrac{1}{2}k) \tag{19}$$

and

$$A_{-k}(n) = A_k(n) \tag{20}$$

The difference of the diagonal elements

$$\Delta(n + \tfrac{1}{2}) = |W(n + 1) - W(n)| \tag{21}$$

will be called the "spacing." For simplicity, we assume all matrix elements to be real, which is true in most birth and death processes. The following assumptions are made for the matrix elements:

I. Regularity assumption; the matrix elements A and the spacings Δ shall be smooth functions of n, i.e.,

$$|A_k(n+1) - A_k(n)| \ll A_k(n), \qquad \text{for all } k \tag{22}$$

$$|\Delta(n+1) - \Delta(n)| \ll \Delta(n) \tag{23}$$

II. Magnitude assumption; for a given n, at least one of the A's shall be large compared with the corresponding spacing, i.e.,

$$|A_k(n + \tfrac{1}{2}k)| \gg |W(n+k) - W(n)|, \qquad \text{for at least one } k \tag{24}$$

The latter property is the origin of the term "large perturbations."

Using a new notation, we can rewrite the eigenvalue equation (13) in the form

$$\psi(n)[W(n) - \lambda] = \sum_{k=M}^{M}{}' \psi(n+k)A_k(n + \tfrac{1}{2}k) \tag{25}$$

where λ is the eigenvalue, M is the maximum number of possible transitions per unit time, and the prime at the sum over k means omission of $k = 0$.

To solve the eigenvalue difference equation (25) we will use the WKB method.

From Eq. (14) the eigenfunction $\psi_0(n)$ corresponding to the lowest eigenvalue $\lambda = 0$ can be rewritten as

$$\psi_0(n) = C_0(n) \exp[\tfrac{1}{2}\Phi_e(n)]$$

where $\Phi_e(n)$, given by Eq. (A.5), is the sum of slowly varying functions of n and $C_0(n)$ is a slowly varying function of n. We will be able to express the eigenfunction $\psi(n)$ in the form

$$\psi(n) = \mathrm{Re}\left[c(n) \exp \int^n f(\nu)\, d\nu\right] \tag{26}$$

where Re means real part, and c and f are assumed to be slowly varying functions of n. Substituting Eq. (26) into Eq. (25), we obtain

$$2 \sum_{k=1}^{M} A_k(n) \cosh[kf(n)] = W(n) - \lambda \tag{27}$$

from the zeroth-order terms of the derivative with respect to n, and

$$c(n) = \gamma \left\{ \sum_{k=1}^{M} kA_k(n) \sinh[kf(n)] \right\}^{-1/2} \tag{28}$$

from the first-order terms, where γ is a constant.

3.1. A Tridiagonal Matrix Case

When only one-step transitions exist, all off-diagonal elements vanish except $A_1(n)$ and the transition matrix Γ is a tridiagonal matrix. The elements shall be subject to the conditions I and II [Eqs. (22)–(24)] and to the convergence condition

$$|A_1(n)| < \tfrac{1}{2}W(n) \qquad \text{near the boundaries} \tag{29}$$

The boundary conditions of $\psi(n)$ are

$$\psi(n_{\text{low}} - 1) = 0, \qquad \psi(n_{\text{up}} + 1) = 0 \tag{30}$$

where n_{low} and n_{up} are the lower and upper limits of n, respectively.

We define a "quasipotential" $V(n)$ by

$$V(n) = [W(n) - \lambda]/2A_1(n) \tag{31}$$

and classify the regions of n into three types by the value of $V(n)$:

$$-1 < V(n) < 1 \tag{32a}$$

$$V(n) > 1 \tag{32b}$$

$$V(n) < -1 \tag{32c}$$

The forms of the eigenfunctions $\psi(n)$ in the different regions are as follows:

(a) In the region of type (32a), the eigenfunction is given by

$$\psi(n) = \gamma[A_1(n) \sin v(n)]^{-1/2} \cos \int v(\nu)\, d\nu \tag{33a}$$

where

$$v(n) = \cos^{-1} V(n) \tag{34a}$$

(b) In the regions of type (32b), the eigenfunction is an exponential function

$$\psi(n) = \gamma[A_1(n) \sinh f(n)]^{-1/2} \exp\left[\pm \int^n f(\nu)\, d\nu \right] \tag{33b}$$

where

$$f(n) = \cosh^{-1} V(n) \tag{34b}$$

(c) In the regions of type (32c), we have the solution

$$\psi(n) = \gamma(-1)^n[A_1(n) \sinh f(n)]^{-1/2} \exp\left[\pm \int^n f(\nu)\, d\nu \right] \tag{33c}$$

where

$$f(n) = \cosh^{-1}|V(n)| \tag{34c}$$

In the regions close to the boundaries, case (b) or (c) occurs because of the convergence condition. The signs of the exponents of Eq. (33b) and (33c) must be chosen to satisfy the boundary condition (30). In the other regions the eigenfunction is of a different form from the expressions (33a)–(33c), depending upon the value of $V(n)$. These different forms of the expression are made continuous by the WKB connection. We will give two examples of the simplest cases.

Example 1. We will consider the simplest case when the regions of $n_{\text{low}} < n < n_1$ and $n_2 < n < n_{\text{up}}$ are that of type (32b), and the region $n_1 < n < n_2$ belongs to the type (32a). From Eq. (33b) we can easily obtain expressions for the eigenfunction as[5]

$$\psi(n) = \begin{cases} \gamma[A_1(n) \sinh f(n)]^{-1/2} \exp\left[-\int_n^{n_1} f(\nu)\, d\nu\right], & n_{\text{low}} < n < n_1 \\ \gamma'[A_1(n) \sinh f(n)]^{-1/2} \exp\left[-\int_{n_2}^{n} f(\nu)\, d\nu\right], & n_{\text{up}} > n > n_2 \end{cases} \tag{35}$$

The WKB connection of Eq. (35) into the region $n_1 < n < n_2$ is

$$\psi(n) = 2\gamma[A_1(n) \sin v(n)]^{-1/2} \cos\left[\int_{n_1}^{n} v(\nu)\, d\nu - \tfrac{1}{4}\pi\right], \qquad n_1 < n < n_2 \tag{36}$$

Then we have two conditions, one of which is a "quantum condition"

$$\int_{n_1}^{n_2} v(n)\, dn = \pi(l + \tfrac{1}{2}), \qquad l = \text{nonnegative integer} \tag{37}$$

to determine the eigenvalue, the other of which is the condition for the two constants

$$\gamma' = (-1)^l \gamma \tag{38}$$

Example 2. The second simplest example is the case when the regions of $n_{\text{low}} < n < n_1$, $n_2 < n < n_3$, and $n_4 < n < n_{\text{up}}$ are of the type (32b) and when the regions of $n_1 < n < n_2$ and $n_3 < n < n_4$ belong to the type (32a).

[5] To satisfy the boundary condition, the correct expressions of the eigenfunction have to be

$$\psi(n) = \begin{cases} \gamma_1[A_1(n) \sinh f(n)]^{-1/2} \sinh\left[\int_{n_{\text{low}}-1}^{n} f(\nu)\, d\nu\right], & n_{\text{low}} \leqslant n < n_1 \\ \gamma_2[A_1(n) \sinh f(n)]^{-1/2} \sinh\left[\int_{n}^{n_{\text{up}}+1} f(\nu)\, d\nu\right], & n_{\text{up}} \geqslant n > n_2 \end{cases}$$

instead of Eq. (35). However, if n_1 and n_2 are macroscopically separated from the boundaries, then we can approximately use Eq. (35) as the eigenfunction. The error of the approximation is of the order of $\exp\left[-\int_{n_{\text{low}}-1}^{n_1} f(n)\, dn\right]$, or $\exp\left[-\int_{n_2}^{n_{\text{up}}+1} f(n)\, dn\right]$.

From the boundary condition, the eigenfunction in the regions of $n_{\text{low}} < n < n_1$ and $n_4 < n < n_{\text{up}}$ is given in the form of Eq. (35). Using the WKB connection to the eigenfunction at each turning point, we can obtain the "quantum" condition

$$\gamma_1 \cos \theta_1 = \gamma_2 e^{-b} \sin \theta_2, \qquad \gamma_1 e^{-b} \sin \theta_1 = \gamma_2 \cos \theta_2 \tag{39}$$

where

$$\theta_1 = \int_{n_1}^{n_2} v(n)\, dn, \qquad \theta_2 = \int_{n_3}^{n_4} v(n)\, dn, \qquad b = \int_{n_2}^{n_3} f(n)\, dn \tag{40}$$

If the region of $n_2 < n < n_3$ is macroscopically wide and is of the order of Ω, it will be a good approximation to consider the two regions of type (32a) as independent "potential wells." Within this approximation we can apply the quantum condition in each region and obtain

$$\theta_1 = (l_1 + \tfrac{1}{2})\pi, \qquad \theta_2 = (l_2 + \tfrac{1}{2})\pi \tag{41}$$

where both l_1 and l_2 are nonnegative integers. Corrections to this approximation become important only when two eigenfunctions localizing at different potential wells are degenerate. This case will be considered in a later section.

3.2. Nontridiagonal Matrix Cases

These cases are more complicated than the previous ones. We will consider only one simple case. The others can be calculated in a straightforward manner.

When there exist one-step and two-step transitions, the off-diagonal matrix elements of $k = 1, 2$ are the only nonvanishing ones. Equation (27) can be written as

$$2A_1(n) \cosh f(n) + 2A_1(n) \cosh 2f(n) = W(n) - \lambda \tag{42}$$

There exists one more type of region in this case than in the previous one. We redefine a quasipotential $V(n)$ by

$$V(n) = \frac{1}{4A_2(n)} \left(-A_1(n) + \{A_1^2(n) + 4A_2(n)[W(n) - \lambda + 2A_2(n)]\}^{1/2}\right) \tag{43}$$

and classify the regions into four types as follows:

(a) $V(n)$ is real and $V(n) < 1$, i.e.,

$$2A_2(n) - 2A_1(n) < W(n) - \lambda < 2A_1(n) + 2A_2(n) \quad \text{if } A_1(n) > 4A_2(n) \tag{44}$$

$$-\frac{A_1^2(n) + 8A_2^2(n)}{4A_2(n)} < W(n) - \lambda < 2A_1(n) + 2A_2(n) \quad \text{if } A_1(n) < 4A_2(n) \tag{45}$$

(b) $V(n)$ is real and $V(n) > 1$, i.e.,

$$W(n) - \lambda > 2A_1(n) + 2A_2(n) \tag{46}$$

(c) $V(n)$ is real and $V(n) < -1$, i.e.,

$$-\frac{A_1^2(n) + 8A_2^2(n)}{4A_2(n)} < W(n) - \lambda < 2A_2(n) - 2A_1(n)$$

$$\text{only if } A_1(n) > 4A_2(n) \tag{47}$$

(d) $V(n)$ is complex, i.e.,

$$W(n) - \lambda < -[A_1^2(n) + 8A_2^2(n)]/4A_2(n) \tag{48}$$

The "wave number" $f(n)$ corresponding to each type of regions (a)–(d) is expressed as follows:

$$u(n) = 0, \qquad \cos v(n) = V(n) \tag{49a}$$

$$\cosh u(n) = V(n), \qquad v(n) = 0 \tag{49b}$$

$$\cosh u(n) = -V(n), \qquad v(n) = \pi \tag{49c}$$

$$\cosh u(n) = \frac{1}{4}\left\{\left[2 - \frac{W-\lambda}{A_2} + \frac{2A_1}{A_2}\right]^{1/2} \pm \left[2 - \frac{W-\lambda}{A_2} - \frac{2A_1}{A_2}\right]^{1/2}\right\}, \quad \begin{matrix} + \text{ if } A_1 < 4A_2 \\ - \text{ if } A_1 > 4A_2 \end{matrix} \tag{49d}$$

$$\cos v(n) = -\frac{A_1}{4A_2 \cosh u(n)}$$

Here $u(n)$ and $v(n)$ are real and imaginary parts of $f(n)$, respectively. The procedure of obtaining the eigenfunction by the WKB connection is the same as that in the previous case, so we will not write down the explicit expression for the eigenfunction. We will show only the quantum condition within the approximation of independent potential wells, which is given by

$$\int_{(a)} v(n)\, dn = \pi(l + c) \tag{50}$$

where (a) indicates the integral is over each region of type (a), l is a non-negative integer, and c is constant. If the region of type (a) is surrounded by those of type (b), then $c = 1/2$.

4. GENERAL ANALYSIS OF EIGENMODES

We will present here a general analysis of the eigenmodes and their eigenvalues. Some of these results have already been presented in a previous paper.[1]

We will give a formula for the density of eigenstates $\rho(\bar{\lambda})$, where $\bar{\lambda} = \epsilon\lambda$ and $\epsilon = \Omega^{-1}$. Most of the eigenmodes have large eigenvalues, of the order of Ω. These modes contribute to the short-term behavior of the relaxation of the system from nonequilibrium initial states. On the other hand, if we focus on the long-time behavior, such as the relaxation of an unstable state or a metastable state, we must analyze in detail the lower lying eigenmodes whose eigenvalues are equal to or less than $O(\Omega^0)$. The lower lying eigenmodes are localized around the stationary states (stable or unstable), in contrast to the other modes, which have an oscillatory behavior over a macroscopic range.

In a critical or marginal case the system shows an anomalous behavior, such as a critical slowing down. Such an anomaly is caused by the divergence of $\rho(\bar{\lambda})$ at $\bar{\lambda} = 0$ which means that a macroscopic number of eigenstates accumulate to the lowest eigenstate in *the thermodynamic limit.*

From the quantum condition given in the last section we can obtain the density of eigenstates as

$$\rho(\bar{\lambda}) = \frac{1}{\pi r_0} \frac{d}{d\bar{\lambda}} \int_{(a)} \cos^{-1} V(x, \bar{\lambda})\, dx \tag{51}$$

where a normalized macrovariable $x = \epsilon r_0 n$ is used and $V(x)$ is expressed by $V(x, \bar{\lambda})$ to show the $\bar{\lambda}$ dependence of V explicitly.

The quasipotential V defined by Eq. (31) or (43) can be written in terms of an ϵ expansion:

(i) Tridiagonal matrix case:

$$V(x, \bar{\lambda}) = \cosh\left[\frac{r_0}{2}\phi_e'(x)\right] - \frac{\bar{\lambda}}{2\mathscr{A}_1(x)} + \frac{\epsilon r_0^2}{4}\phi_e''(x)\cosh\left[\frac{r_0}{2}\phi_e'(x)\right] + \frac{\epsilon r_0}{2}\frac{\mathscr{A}_1'(x)}{\mathscr{A}_1(x)}\sinh\left[\frac{r_0}{2}\phi_e'(x)\right] + O(\epsilon^2) \tag{52}$$

(ii) Pentadiagonal matrix case:

$$\begin{aligned} V(x, \bar{\lambda}) = {} & \cosh[\tfrac{1}{2}r_0\phi_e'(x)] - \tfrac{1}{2}\bar{\lambda}\{\mathscr{A}_1(x) + 4\mathscr{A}_2(x)\cosh[\tfrac{1}{2}r_0\phi_e'(x)]\}^{-1} \\ & + \tfrac{1}{4}\epsilon r_0^2\phi_e''(x)\cosh[\tfrac{1}{2}r_0\phi_e'(x)] + \tfrac{1}{2}\epsilon r_0\sinh[\tfrac{1}{2}r_0\phi_e'(x)] \\ & \times \{2r_0^2\mathscr{A}_2(x)\phi_e''(x)\sinh[\tfrac{1}{2}r_0\phi_e'(x)] \\ & + \mathscr{A}_1'(x) + 4\mathscr{A}_2'(x)\cosh[\tfrac{1}{2}r_0\phi_e'(x)]\} \\ & \times \{\mathscr{A}_1(x) + 4\mathscr{A}_2(x)\cosh[\tfrac{1}{2}r_0\phi_e'(x)]\}^{-1} + O(\epsilon^2) \end{aligned} \tag{53}$$

Here normalized matrix elements $\mathscr{A}_k(x) = (1/\epsilon)A_k(x/\epsilon r_0)$ $(k = 1, 2)$ are used. Substituting the lowest order term of Eq. (52) or (53) into Eq. (51), we will obtain the formula of the density of eigenstates as follows:

(i) Tridiagonal matrix case:

$$\rho(\bar{\lambda}) = \frac{1}{\pi r_0}\int dx\left[2\mathscr{A}_1\left(1 + \cosh\frac{r_0}{2}\phi_e'\right) - \bar{\lambda}\right]^{1/2} \times \left[2\mathscr{A}_1\left(1 - \cosh\frac{r_0}{2}\phi_e'\right) + \bar{\lambda}\right]^{-1/2} \tag{54}$$

(ii) Pentadiagonal matrix case:

$$\rho(\bar{\lambda}) = \frac{1}{2\pi r_0}\int dx\, \mathscr{A}_2^{-1/2}\left[2\left(\mathscr{A}_1 + 4\mathscr{A}_2\cosh\frac{r_0}{2}\phi_e'\right)\left(1 + \cosh\frac{r_0}{2}\phi_e'\right) - \bar{\lambda}\right]^{-1/2} \times \left[2\left(\mathscr{A}_1 + 4\mathscr{A}_2\cosh\frac{r_0}{2}\phi_e'\right)\left(1 - \cosh\frac{r_0}{2}\phi_e'\right) + \bar{\lambda}\right]^{-1/2} \times \left[\frac{1}{4\mathscr{A}_2}\left(\mathscr{A}_1 + 4\mathscr{A}_2\cosh\frac{r_0}{2}\phi_e'\right)^2 - \bar{\lambda}\right]^{-1/2} \times \left(\mathscr{A}_1 + 4\mathscr{A}_2\cosh\frac{r_0}{2}\phi_e'\right) \tag{55}$$

Here the integrations in Eqs. (54) and (55) have to be done over all regions of type (a).

Using the expansion form of $\phi_e(x)$ around each stationary state $x = x_s^{(i)}$

$$\phi_e(x) = C_0^{(i)} - \tfrac{1}{2}C_1^{(i)}(x - x_s^{(i)})^2 - \tfrac{1}{3}C_2^{(i)}(x - x_s^{(i)})^3 - \tfrac{1}{4}C_3^{(i)}(x - x_s^{(i)})^4 \cdots \tag{56}$$

we can classify the stationary states $x_s^{(i)}$ by the coefficients:

(a) A stable equilibrium, $C_1^{(i)} > 0$.
(b) An unstable equilibrium, $C_1^{(i)} < 0$.
(c) A marginal equilibrium, $C_1^{(i)} = 0$ and $C_2^{(i)} \neq 0$.
(d) A critical equilibrium, $C_1^{(i)} = 0$, $C_2^{(i)} = 0$, and $C_3^{(i)} \neq 0$.

From Eqs. (54) and (55) we obtain the asymptotic form of $\rho(\bar{\lambda})$ at $\bar{\lambda} = 0$ as

$$\rho(\bar{\lambda}) \simeq \sum_i D_m^{(i)}\bar{\lambda}^{(1-m)/2m} \tag{57}$$

in both cases, where

$$D_m^{(i)} = \frac{m+1}{2m}\, 2^{(1-m)/m}[r_0{}^2\mathscr{A}_1(x_s^{(i)})]^{-(m+1)/2m}|C_m^{(i)}|^{-1/m}B_m \tag{58}$$

and where the sums must be carried out over all stationary states. The type of each stationary state is denoted by $m = 1$, 2, or 3 corresponding to the case (a), (b), (c), or (d). The constant B_m is given below in Eq. (73). The

derivation of Eq. (57) will be given in a later part of this section. From Eq. (57) we can conclude that in a case when the system has a critical equilibrium ($m = 3$) the density of eigenstates diverges at $\bar{\lambda} = 0$ such that

$$\rho(\bar{\lambda}) \propto \bar{\lambda}^{-1/3}, \qquad \bar{\lambda} \to 0 \tag{59}$$

and that in a case when the system has a marginal equilibrium ($m = 2$)

$$\rho(\bar{\lambda}) \propto \bar{\lambda}^{-1/4}, \qquad \bar{\lambda} \to 0 \tag{60}$$

In some cases the divergence of $\rho(\bar{\lambda})$ occurs at a finite value of $\bar{\lambda}$, but such divergence does not correspond to any thermodynamic phenomena.

We will now consider the lower lying eigenmodes. In this case the eigenvalue λ is equal to or greater than $O(\epsilon^0)$, so we have to take the terms of the order of ϵ in Eq. (52) or (53). If we take the lowest order terms in the Taylor expansion of $V(x)$ around $x_s^{(i)}$, we will have the same equation

$$V(x) = 1 - \frac{\epsilon\lambda}{2\mathscr{A}_1(x_s^{(i)})} - \frac{\epsilon k {r_0}^2 C_m^{(i)}}{4}(x - x_s^{(i)})^{m-1} + \frac{{r_0}^2[C_m^{(i)}]^2}{8}(x - x_s^{(i)})^{2m} \tag{61}$$

in both cases. Here $m = 1$, 2, or 3, corresponding to the case (a), (b), (c), or (d).

Within the approximation of the independent potential wells, the quantum condition can be written as

$$\int_{x_1}^{x_2} \frac{xV(x)}{\{1 - [V(x)]^2\}^{1/2}}\, dx = \pi\epsilon r_0\left(l + \frac{1}{2}\right) \tag{62}$$

at each potential well. Here the integration limits are determined by

$$V(x_1) = V(x_2) = 1 \tag{63}$$

From Eq. (61) we have the relations

$$|x_{1,2} - x_s^{(i)}| = O(\epsilon^{1/(m+1)}) \tag{64}$$

$$V(x) = 1 - O(\epsilon), \qquad x_1 < x < x_2 \tag{65}$$

Equation (62) can be approximated by

$$\sqrt{2}\int_{x_1}^{x_2} [1 - V(x)]^{1/2}\, dx = \pi\epsilon r_0(l + \tfrac{1}{2}) \tag{66}$$

In the case of $m = 1$, we can easily integrate Eq. (66) and obtain the expression for the eigenvalues as

$$\lambda_l^{(i)} = {r_0}^2\mathscr{A}_1(x_s^{(i)})|C_1^{(i)}|l \qquad \text{for } m = 1 \tag{67}$$

where

$$l = \begin{cases} 0, 1, 2, 3,... & \text{for } C_1^{(i)} > 0 \\ 1, 2, 3, 4,... & \text{for } C_1^{(i)} < 0 \end{cases} \tag{68}$$

In the cases of $m = 2, 3$, we use the variables transformed by

$$\lambda = \xi\epsilon^{(m-1)/(m+1)}, \qquad x - x_s^{(i)} = \epsilon^{1/(m+1)}\left[\frac{4\xi}{r_0{}^2[C_m^{(i)}]^2\mathscr{A}_1(x_s^{(i)})}\right]^{1/2m}\eta \tag{69}$$

Then we can write Eq. (66) in the form

$$2\int_{\eta_1}^{\eta_2}[1 + mS\eta^{m-1}\,\mathrm{sgn}(C_m^{(i)}) - \eta^{2m}]^{1/2}\,d\eta = 2\pi S(l + \tfrac{1}{2}) \tag{70}$$

where

$$S = 2[r_0{}^2\mathscr{A}_1(x_s^{(i)})/4\xi]^{(m+1)/2m}|C_m^{(i)}|^{1/m} \tag{71}$$

If ξ is sufficiently large, we can neglect the term including S in the integrand of Eq. (52), and obtain the simple expression for the eigenvalues as

$$\lambda_l^{(i)} \simeq \epsilon^{(m-1)/(m+1)}l^{2m/(m+1)}r_0{}^2\mathscr{A}_1(x_s^{(i)})(\tfrac{1}{2}|C_m^{(i)}|)^{2/(m+1)}(2\pi/B_m)^{2m/(m+1)} \tag{72}$$

where

$$B_m = 4\int_0^1 (1 - \eta^{2m})^{1/2}\,d\eta \tag{73}$$

The constants B_m ($m = 2, 3$) are expressed by the use of the first kind of the entire elliptic integral $K(k)$ as

$$B_2 = \frac{4\sqrt{2}}{3}K\left(\frac{1}{\sqrt{2}}\right) = 3.496... \tag{74}$$

$$B_3 = 3K\left(\frac{\sqrt{6} - \sqrt{2}}{4}\right) = 4.794... \tag{75}$$

When the integer l in Eq. (72) is sufficiently large, the neglect of the terms in going from (70) to (72) can be justified. The expressions for the eigenvalues are obtained as

$$\lambda_l^{(m)} \propto \epsilon^{1/3}l^{4/3} \qquad \text{in a marginal case} \tag{76}$$

$$\lambda_l^{(c)} \propto \epsilon^{1/2}l^{3/2} \qquad \text{in a critical case} \tag{77}$$

The asymptotic form of $\rho(\bar{\lambda})$ at $\bar{\lambda} = 0$ is derived from Eq. (72). From (77) [or (76)] we can conclude that the number of the lower lying eigenmodes is of the order of $\Omega^{1/3}$ (or $\Omega^{1/4}$) in a critical (or marginal) case.

In the case when the system differs infinitesimally from the critical or marginal case, how many lower lying eigenmodes exist? To answer the question we will investigate three cases (Fig. 1). In each case the coefficients of Eq. (56) can be taken as follows:

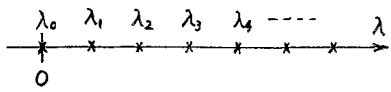

Fig. 1a. The distribution of the lower lying eigenvalues when a system has only one stable equilibrium.

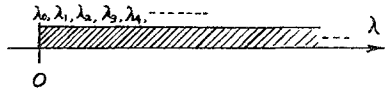

Fig. 1b. The distribution of the lower lying eigenvalues when a system is critical, marginal, or infinitesimally close to a critical (or marginal) state. The distribution is discrete for a finite system and becomes a continuum in the thermodynamic limit.

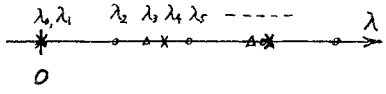

Fig. 1c. The distribution of the lower lying eigenvalues when a system has one stable, one metastable, and one unstable equilibrium. The eigenvalues whose eigenmodes are localized mainly at the stable, metastable, and unstable equilibria are denoted by ×, △, and ○, respectively.

(I) The cases infinitesimally close to a critical one:

$$\text{(a)}\quad C_1 = \epsilon^{\delta} d_1, \qquad C_2 = 0, \qquad C_3 = O(\epsilon^0) \neq 0 \tag{78}$$

$$\text{(b)}\quad C_1 = 0, \qquad C_2 = \epsilon^{\rho} d_2, \qquad C_3 = O(\epsilon^0) \neq 0 \tag{79}$$

(II) The case infinitesimally close to a marginal one:

$$C_1 = \epsilon^{\delta} d_1, \qquad C_2 = O(\epsilon^0) \neq 0 \tag{80}$$

In case (Ia), Eq. (61) is given by

$$V(x) = 1 - \frac{\epsilon\lambda}{2\mathscr{A}_1(x_s)} - \epsilon^{1+\delta}\frac{{r_0}^2 d_1}{4} - \left(\epsilon\frac{3{r_0}^2 C_3}{4} - \epsilon^{2\delta}\frac{{r_0}^2 {d_1}^2}{8}\right)(x - x_s)^2 + \frac{{r_0}^2 {C_3}^2}{8}(x - x_s)^6 \tag{81}$$

Using the transformation

$$x - x_s = \eta\epsilon^{\sigma}$$

and comparing the order of the terms in the integrand of Eq. (66), we will have two cases:

(i) The case when $0 < \delta < \frac{1}{2}$:

$$\delta + 2\sigma = 1, \qquad \lambda = \xi\epsilon^{-\delta}$$

(ii) The case when $\delta > \frac{1}{2}$:

$$\sigma = \tfrac{1}{4}, \qquad \lambda = \xi\epsilon^{-1/2}$$

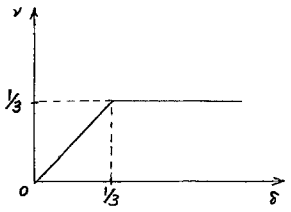

Fig. 2. The exponent ν as a function of the exponent δ for case I(a).

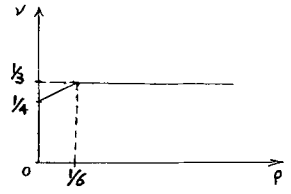

Fig. 3. The exponent ν as a function of the exponent ρ for case I(b).

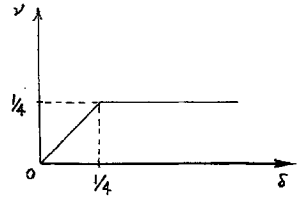

Fig. 4. The exponent ν as a function of the exponent δ for case II.

In the former case the expression for the eigenvalue is given by

$$\lambda_l \propto \epsilon^{\delta} l$$

The latter case reduces to the critical one. In case (i) we have to treat carefully the terms of Eq. (81) when λ is $O(\epsilon^0)$, i.e., l is $O(\epsilon^{-\delta})$. At this time the higher power terms become dominant when $\frac{1}{3} < \delta < \frac{1}{2}$. We denote here by Ω^{ν} the order of the number $O(\ell)$ of lower lying eigenvalues, where $O(\lambda_l) \leqslant O(\Omega^0)$ for $l = 1, 2, 3, \ldots, \ell$. The exponent ν can be obtained as a function of δ (see Fig. 2).

Using similar procedures, we can express the exponent ν as a function of δ or ρ in the other cases. The results are shown in Figs. 3 and 4.

5. RELAXATION TIMES OF METASTABLE AND UNSTABLE STATES

In this section we discuss the relaxation times from metastable and unstable states. As we have shown in the last section, the quasipotential $V(x)$ has a well at each stationary state even if the state is unstable. However, all eigenmodes localized near the unstable state have finite eigenvalue, so they decay for sufficiently long time. On the other hand, each stable state has one eigenmode with a zero eigenvalue within the approximation of the independent potential wells. In other words, there exists n-fold degeneracy

in the lowest eigenmode, where n is the number of stable states. Within our approximation we cannot distinguish between metastable states and a stable one. We therefore have to find the correct lower lying eigenmodes by considering corrections to our approximation.

For simplicity, we will consider the case when a system has one unstable state x_u, one metastable state x_m, and one stable state x_e. Other cases can be calculated by applying the method presented below.

We already know that the true lowest eigenmode $\psi_0(x)$ is nondegenerate and given by Eq. (14). It has two peaks, one at $x = x_e$ and one at x_m. The ratio of the heights of these peaks is given by

$$[\mathscr{A}_1(x_m)/\mathscr{A}_1(x_e)]^{1/2} \exp[(1/2\epsilon)(\Delta_e - \Delta_m)] \tag{82}$$

where Δ_e and Δ_m denote the free energy barrier of the stable state and that of the unstable state, respectively, i.e.,

$$\Delta_e = \phi_e(x_e) - \phi_e(x_u), \qquad \Delta_m = \phi_e(x_m) - \phi_e(x_u) \tag{83}$$

Using Eq. (39) and the properties of $\psi_0(x)$, we obtain the following solutions of Eq. (40):

$$\gamma_1 = \gamma_2 \left[\frac{C_1(x_e)}{C_1(x_m)}\right]^{1/2} \exp\left[\frac{1}{2\epsilon}(\Delta_e - \Delta_m)\right] \tag{84}$$

$$e^b = \left[\frac{\mathscr{A}_1(x_e)\mathscr{A}_2(x_m)}{\mathscr{A}_1{}^2(x_u)}\right]^{1/2} \left[\frac{C_1(x_e)C_1(x_m)}{C_1{}^2(x_u)}\right]^{1/4} \exp\left[\frac{1}{2\epsilon}(\Delta_e + \Delta_m)\right] \tag{85}$$

$$\theta_1(\lambda_0) = \frac{\pi}{2} - \left[\frac{\mathscr{A}_1{}^2(x_u)}{\mathscr{A}_1(x_e)\mathscr{A}_1(x_m)}\right]^{1/2} \left[\frac{C_1{}^2(x_u)C_1(x_m)}{C_1{}^3(x_e)}\right]^{1/4} e^{-\Delta I_e \epsilon}, \tag{86}$$

$$\theta_2(\lambda_0) = \frac{\pi}{2} - \left[\frac{\mathscr{A}_1{}^2(x_u)}{\mathscr{A}_1(x_e)\mathscr{A}_1(x_u)}\right]^{1/2} \left[\frac{C_1{}^2(x_u)C_1(x_e)}{C_1{}^3(x_m)}\right]^{1/4} e^{-\Delta_m/\epsilon} \tag{87}$$

where $x_1 < x_e < x_2$, $x_3 < x_m < x_4$, and $\theta_i(\lambda)$ is used to show the λ dependence of θ_i.

The second lowest eigenmode $\psi_1(x)$ can easily be constructed because it has one node and is orthogonal to $\psi_0(x)$. The solutions of Eq. (40) are given by

$$\gamma_1 = -\gamma_2 \left[\frac{\mathscr{A}_1(x_e)}{\mathscr{A}_1(x_m)}\right]\left[\frac{C_1(x_e)}{C_1(x_m)}\right]^{1/2} \exp\left[-\frac{1}{2\epsilon}(\Delta_e - \Delta_m)\right] \tag{88}$$

$$e^b = [\text{the same as Eq. (85)}]$$

$$\theta_1(\lambda_1) = \frac{\pi}{2} + \left[\frac{\mathscr{A}_1{}^2(x_u)\mathscr{A}_1(x_m)}{\mathscr{A}_1{}^3(x_e)}\right]^{1/2} \left[\frac{C_1{}^2(x_u)C_1(x_m)}{C_1{}^3(x_e)}\right]^{1/4} e^{-\Delta_m/\epsilon} \tag{89}$$

$$\theta_2(\lambda_1) = \frac{\pi}{2} + \left[\frac{\mathscr{A}_1{}^2(x_u)\mathscr{A}_1(x_e)}{\mathscr{A}_1{}^3(x_m)}\right]^{1/2} \left[\frac{C_1{}^2(x_u)C_1(x_e)}{C_1{}^3(x_m)}\right]^{1/4} e^{-\Delta_e/\epsilon} \tag{90}$$

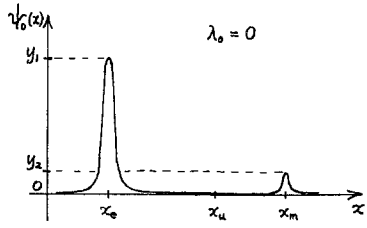

Fig. 5. The shape of the lowest eigenmode $\psi_0(x)$, where $y_1 = O(\epsilon^{-1/4})$ and $Y_2 = O\{\epsilon^{-1/4} \exp[-(1/2\epsilon)(\Delta_e - \Delta_m)]\}$.

Using Eqs. (86), (87), (89), and (90) and taking into account that $\lambda_0 = 0$ and $(d^n/d\lambda^n)\theta_i(\lambda) = 0$ $(n \geqslant 2)$, we obtain

$$\lambda_1 = \frac{{r_0}^2}{\pi} \mathscr{A}_1(x_u)[{C_1}^2(x_u)C_1(x_e)C_1(x_m)]^{1/4}$$

$$\times \left\{ \left[\frac{\mathscr{A}_1(x_m)}{\mathscr{A}_1(x_e)}\right]^{1/2} e^{-\Delta_m/\epsilon} + \left[\frac{\mathscr{A}_1(x_e)}{\mathscr{A}_1(x_m)}\right]^{1/2} e^{-\Delta_e/\epsilon} \right\} \tag{91}$$

This result shows that the second lowest eigenvalue λ_1 is of the order of $e^{-\Delta_m/\epsilon}$.

We can easily show that the third lowest eigenmode $\psi_2(x)$ is usually localized mainly at the unstable state. The rough shapes of the three lowest eigenmodes are given in Figs. 5–7.

Now we consider the relaxation times of unstable and metastable states. The nonequilibrium probability distribution $P(x, t)$ has been expressed by the eigenmodes in Eq. (17). If we focus on the long-time behavior, it becomes a good approximation to take only the lower lying eigenmodes.

First we will obtain the relaxation time τ_u of an unstable state. In this case we can take the three lowest eigenmodes ψ_0, ψ_1, and ψ_2 at a sufficiently long time. The lowest eigenvalue of the eigenmode localized mainly around the unstable state is λ_2, so that the τ_u is given by

$$\tau_u = 1/\lambda_2 = [{r_0}^2 \mathscr{A}_1(x_u)|C_1(x_u)|]^{-1} \tag{92}$$

For an initial δ-function distribution

$$P(x, 0) = \delta(x - x_u) \tag{93}$$

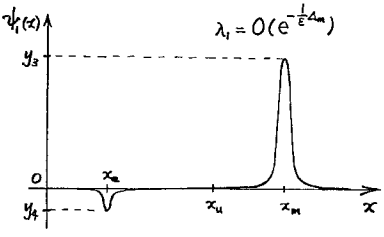

Fig. 6. The shape of the second lowest eigenmode $\psi_1(x)$, where $y_3 = O(\epsilon^{-1/4})$ and $|y_4| = O\{\epsilon^{-1/4} \exp[(1/2\epsilon)(\Delta_e - \Delta_m)]\}$.

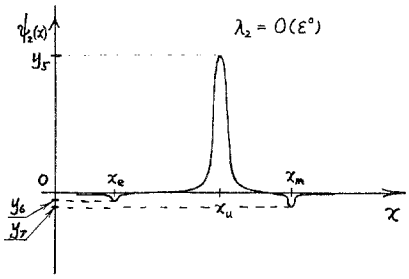

Fig. 7. The shape of the third lowest eigenmode $\psi_2(x)$, where $y_5 = O(\epsilon^{-1/4})$, $|y_6| = O\{\epsilon^{-1/4} \exp[-(1/2\epsilon)\,\Delta_e]\}$, and $|y_7| = O\{\epsilon^{-1/4} \exp[-(1/2\epsilon)\,\Delta_m]\}$.

the coefficients p_1 and p_2 in Eq. (17) will be $O(e^{(\Delta_e - \Delta_m)/2\epsilon})$ and $O(e^{\Delta_e/2\epsilon})$, respectively, and $P(x, t)$ at $x = x_u$ is given by

$$P(x_u, t) = O(\epsilon^{-1/2} e^{-\lambda_2 t}) \tag{94}$$

At time τ_u, $P(x, t)$ extends uniformly over the metastable and stable states. After the time τ_u, $P(x, t)$ has peaks at the metastable and stable states and can be written as

$$P(x, t) = P_e(x) + p_1 p_e^{1/2}(x)\psi_1(x) \tag{95}$$

At times $t \gg \tau_u$, the metastable state also will have relaxed.

It must be mentioned that the time τ_ℓ discussed by Kubo *et al.*[1] and others,[10] is not the relaxation time of the unstable state in the usual sense, where

$$\tau_\ell = -(1/2\lambda_2) \ln \epsilon \tag{96}$$

At time τ_ℓ, $P(x, t)$ already has had peaks of $O(\epsilon^{-1/2})$ at metastable and stable states and its plateau expanding over the metastable and stable states is only of $O(\epsilon^0)$.

Second, we consider the relaxation time τ_m of the metastable state. The relaxation time of the eigenmode $\psi_1(x)$ is much longer than that of the other eigenmodes localized mainly around the metastable state. Therefore, we can conclude that the relaxation time τ_m is equal to that of ψ_1, i.e.,

$$\tau_m = 1/\lambda_1 = O(e^{\Delta_m/\epsilon}) \tag{97}$$

where λ_1 is given by Eq. (91). At times $t \gg \tau_m$, one then has

$$P(x, t) \simeq P_e(x) \tag{98}$$

6. SOME EXAMPLES

We have analyzed general nonlinear birth and death processes in the previous sections. In this section we will take two specific examples and

show how our analysis works. As the first example we consider a kinetic Weiss–Ising model in which phase transitions occur. The second example is a stochastic model for a nonlinear chemical reaction with one variable.

In order to verify the accuracy of the general analysis we have compared our approximate results with the exact results obtained for the Alkemade diode.[11,12] This comparison showed that our approximate analysis was in good agreement with the exact results for Ω large.

6.1. A Kinetic Weiss–Ising Model[1,13,14]

The model is a birth and death process of a system composed of N Ising spins. The transition probabilities of the spin flip are assumed to be

$$\begin{aligned} W(N_+ - N_-, -2) &= N_+ \exp\left[-\mu - \frac{\alpha}{N}(N_+ - N_-)\right] \\ W(N_+ - N_-, +2) &= N_- \exp\left[\mu + \frac{\alpha}{N}(N_+ - N_-)\right] \end{aligned} \tag{99}$$

for one-flip transitions and

$$\begin{aligned} W(N_+ - N_-, -4) &= \frac{N_+(N_+ - 1)}{N} \exp\left[-2\mu - \frac{2\alpha}{N}(N_+ - N_-)\right] \\ W(N_+ - N_-, +4) &= \frac{N_-(N_- - 1)}{N} \exp\left[2\mu + \frac{2\alpha}{N}(N_+ - N_-)\right] \end{aligned} \tag{100}$$

for two-flip transitions, where N_+ and N_- are the numbers of plus spins and minus spins, respectively, and where the external magnetic field μ and the molecular field coefficient α are scaled by temperature

$$\mu = \mu_0 H/kT, \qquad \alpha = J/kT$$

The free-energy-like function $\phi_e(x)$ is found to be

$$\phi_e(x) = \text{const} + \mu x + \frac{\alpha}{2}x^2 - \frac{1+x}{2}\ln(1+x) - \frac{1-x}{2}\ln(1-x) \tag{101}$$

where $x = (N_+ - N_-)/N$ and $-1 \leqslant x \leqslant 1$.

The equilibrium states are given by solutions of the equation

$$x = \tanh(\mu + \alpha x) \tag{102}$$

In a ferromagnetic region there are three solutions for Eq. (102), two of which are stable (or metastable) and are denoted by x_e (or x_m) and one of which is unstable, x_u. In a paramagnetic region only one stable solution exists and is denoted by x_e.

The off-diagonal elements of the transition matrix Γ, $\mathscr{A}_1(x)$ and $\mathscr{A}_2(x)$, are given by

$$\mathscr{A}_1(x) = \tfrac{1}{2}(1 - x^2)^{1/2} \tag{103}$$

$$\mathscr{A}_2(x) = \tfrac{1}{4}(1 - x^2) \tag{104}$$

If we consider the case (i) when only one-flip transitions occur, i.e., $\mathscr{A}_2(x) = 0$, the diagonal elements $w(x)$ and the quasipotential $V(x)$ are given by

$$w(x) = \cosh(\mu + \alpha X) - x \sinh(\mu + \alpha X) \equiv g(x) \tag{105}$$

$$V(x) = \frac{w(x) - \bar{\lambda}}{[(1 + \epsilon)^2 - x^2]^{1/2} e^{-\alpha\epsilon}} \tag{106}$$

In the case (ii) when both one-flip and two-flip transitions exist, the transition matrix Γ becomes a pentadiagonal matrix, and $w(x)$ and $V(x)$ are given by

$$w(x) = \cosh(\mu + \alpha x) - x \sinh(\mu + \alpha x) + \frac{1 + x^2}{2} \cosh(2\mu + 2\alpha x) - x \sinh(2\mu + 2\alpha x) \tag{107}$$

$$V(x) = (1 - x^2)^{-1/2} e^{\alpha\epsilon} \left(-\frac{1}{2} + \left\{ \frac{1}{4} + \frac{1}{2}(1 - x^2) e^{-2\alpha\epsilon} + \frac{(1 - x^2)^{1/2}}{[(1 + \epsilon)^2 - x^2]^{1/2}} [w(x) - \bar{\lambda}] \right\}^{1/2} \right) \tag{108}$$

The lower lying eigenmodes are common for both cases. From Eq. (67) we can obtain the lower lying eigenvalues of this model as

$$\lambda_l^{(i)} = \begin{cases} 2(l + \delta_{i,u}) \dfrac{|\alpha x_i^2 - \alpha + 1|}{(1 - x_i^2)^{1/2}}, & i = e, m, u \quad \text{ferromagnetic region} \\ 2l \dfrac{\alpha x_i^2 - \alpha + 1}{(1 - x_i^2)^{1/2}}, & i = e \quad \text{paramagnetic region} \end{cases} \tag{109}$$

where l is a nonnegative integer and $\delta_{i,u}$ is the Kronecker delta.

For critical and marginal states we obtain the following expressions for the eigenvalues from Eq. (72):

$$\lambda_l^{(c)} = \tfrac{1}{3}\sqrt{6}(2\pi/B_3)^{3/2} \epsilon^{1/2} l^{3/2} \qquad \text{critical state } (\alpha = 1, \mu = 0) \tag{110}$$

$$\lambda_l^{(m)} = 2^{1/3}(\alpha - 1)^{1/3}(2\pi/B_2)^{4/3} \epsilon^{1/3} l^{4/3} \qquad \text{marginal state } (\alpha > 1, \mu = \mu_c) \tag{111}$$

Here B_2 and B_3 are given by Eqs. (74) and (75), respectively, and

$$\mu_c = -[\alpha(\alpha - 1)]^{1/2} + \frac{1}{2}\ln\frac{\alpha^{1/2} + (\alpha - 1)^{1/2}}{\alpha^{1/2} - (\alpha - 1)^{1/2}} \tag{112}$$

The expressions for the density of eigenstates are different for the two cases. In case (i) we obtain from Eq. (54) that

$$\rho(\bar{\lambda}) = \frac{1}{2\pi}\int dx\,[(1 - x^2)^{1/2} + g(x) - \bar{\lambda}]^{-1/2}[(1 - x^2)^{1/2} - g(x) + \bar{\lambda}]^{-1/2} \tag{113}$$

Using Eq. (55) we can express $\rho(\bar{\lambda})$ for case (ii) as

$$\rho(\bar{\lambda}) = \frac{1}{4\pi}\int dx\left[(1 - x^2)^{1/2} + g(x) - \frac{\bar{\lambda}}{1 + 2g(x)}\right]^{-1/2} \times \left[(1 - x^2)^{1/2} - g(x) + \frac{\bar{\lambda}}{1 + 2g(x)}\right]^{-1/2}\left[\frac{1 + 2g(x)}{2(1 - x^2)^{1/2}} - \bar{\lambda}\right]^{-1/2} \tag{114}$$

where the function $g(x)$ is defined in Eq. (105).

The integration of Eq. (113) or (114) has to be performed numerically. In case (i) the results of Eqs. (109) and (113) have also been obtained by Ruijgrok and Tjon by use of a spin operator algebra.[14] The integration of Eq. (113) was carried out numerically for some cases and the shapes of $\rho(\bar{\lambda})$ are presented in Ref. 14.

In the ferromagnetic region with the magnetic field $\mu > 0$, the state x_m is metastable and x_u is unstable. From Eqs. (92) and (97) the relaxation times of these two states are given by

$$\tau_u = \frac{(1 - x_u^2)^{1/2}}{2|\alpha x_u^2 - \alpha + 1|} \tag{115}$$

$$\tau_m = \frac{\pi}{2}(1 - x_e^2)^{1/2}|\alpha x_u^2 - \alpha + 1|^{1/2} \times (\alpha x_e^2 - \alpha + 1)^{1/4}(\alpha x_m^2 - \alpha + 1)^{1/4}e^{N\Delta_m} \tag{116}$$

where Δ_m is given by Eqs. (101) and (83).

The result of Eq. (116) differs from that obtained by Griffiths *et al.*[13] by a small numerical factor. Their calculation was made on the basis of the Gaussian approximation.

6.2. A Stochastic Model for a Nonlinear Chemical Reaction

There are many different types of chemical reactions even within a one-variable system (see, e.g., Ref. 15). Since we cannot discuss all of them

in this paper, we choose the following nonlinear chemical reaction as a specific example[16]:

$$\begin{gathered} A + 2X \underset{k_2}{\overset{k_1}{\rightleftarrows}} 3X \\ A \underset{k_4}{\overset{k_3}{\rightleftarrows}} X \end{gathered} \tag{117}$$

The concentration of the reactant A is taken to be constant as part of an infinite reservoir. We formulate the stochastic rate equations for this reaction in the standard way.[15] The probability distribution $P(n_X, t)$ obeys the master equation (1), the transition probabilities of which are given by

$$W(n_X, 1) = (k_1/\Omega^2)n_A(n_X - 1)n_X + k_3 n_A \tag{118}$$

$$W(n_X, -1) = (k_2/\Omega^2)n_X(n_X - 1)(n_X - 2) + k_4 n_X \tag{119}$$

Here the number of molecules A and X are given, respectively, by n_A and n_X and the volume dependence of the reaction rates is shown explicitly.

From (A.6) in the appendix we obtain the free-energy-like function $\phi_e(x)$,[6]

$$\phi_e'(x) = \ln \frac{(k_1x^2 + k_3)a}{(k_2x^2 + k_4)x} \tag{120}$$

$$\begin{aligned} \phi_e(x) = \text{const} + x\left(\ln \frac{k_1 a}{k_2} + 1\right) - x \ln x + x \ln \frac{k_1x^2 + k_3}{k_2x^2 + k_4} \\ + 2\left(\frac{k_3}{k_4}\right)^{1/2} \tan^{-1}\left[\left(\frac{k_1}{k_3}\right)^{1/2} x\right] - 2\left(\frac{k_4}{k_2}\right)^{1/2} \tan^{-1}\left[\left(\frac{k_2}{k_4}\right)^{1/2} x\right] \end{aligned} \tag{121}$$

where $a = n_A/\Omega$ and $x = n_X/\Omega$.

The extrema of $\phi_e(x)$ are located at the real, positive solutions of the cubic equation

$$k_2x^3 - k_1ax^2 + k_4x - k_3a = 0 \tag{122}$$

All cases, such as the one-stable-equilibrium case, a marginal case, a critical case, a case with two stable states and one unstable state, etc., occur depending upon the values of the rate constants k_2 through k_4 and the initial concentration of A.

[6] In chemical kinetics the free-energy-like function $\phi_e(x)$ should not be confused with the equilibrium free energy of chemical reaction. The former is defined by the equilibrium probability distribution of the number of molecules considered in the stochastic model. The latter is related to the ratio of the rate coefficients through the equilibrium constant.

We define a constant D by

$$D = 4k_1{}^3k_3a^4 - k_1{}^2k_4{}^2a^2 + 27k_2{}^2k_3{}^2a^2 - 18k_1k_2k_3k_4a^2 + 36k_2k_4{}^3 \quad (123)$$

and distinguish the following cases:

(i) If $D > 0$, there is one real, positive solution x_e of Eq. (122), and the state $x = x_e$ is stable.

(ii) If $D = 0$, there is one triple root x_c of Eq. (122), and the state $x = x_c$ is critical.

(iii) If $D < 0$, there are three real, positive solutions x_1, x_2, and x_3 of Eq. (122), where $x_1 < x_2 < x_3$. The state $x = x_2$ is unstable, and of the states $x = x_1$ and x_3 is stable and the other is metastable depending upon the value of the parameters above. For simplicity, we assume that x_1 is metastable. The marginal case also occurs, but we do not discuss it.

The off-diagonal elements $\mathscr{A}_1(x)$ and the quasipotential $V(x)$ are given by

$$\mathscr{A}_1(x) = (k_1ax^2 + k_3a)^{1/2}(k_2x^3 + k_4x)^{1/2} \quad (124)$$

$$V(x) = \frac{k_2x(x-\epsilon)(x-2\epsilon) + k_1ax(x-\epsilon) + k_4x + k_3a - \bar{\lambda}}{2[k_1a(x-\frac{3}{2}\epsilon)(x-\frac{1}{2}\epsilon) + k_3a]^{1/2}} \times [k_2(x^2 - \tfrac{1}{4}\epsilon^2)(x-\tfrac{3}{2}\epsilon) + k_4(x+\tfrac{1}{2}\epsilon)]^{1/2} \quad (125)$$

where $\epsilon = \Omega^{-1}$.

The lower lying eigenvalues are obtained from Eq. (67) as

$$\lambda_l = \frac{k_1k_2x_e{}^4 + 3k_2k_3x_e{}^2 - k_1k_4x_e{}^2 + k_3k_4}{k_1x_e{}^2 + k_3}\, l \qquad \text{case (i)} \quad (126)$$

$$\lambda_l^{(c)} = \sqrt{2}k_2x_c^{3/2}(2\pi/B_3)^{3/2}\epsilon^{1/2}l^{3/2} \qquad \text{case (ii)} \quad (127)$$

$$\left.\begin{aligned} \lambda_l^{(e)} &= k_2(x_e - x_u)(x_e - x_m)l \\ \lambda_l^{(u)} &= k_2(x_e - x_u)(x_u - x_m)(l+1) \\ \lambda_l^{(m)} &= k_2(x_e - x_m)(x_u - x_m)l \end{aligned}\right\} \qquad \text{case (iii)} \quad (128)$$

From Eqs. (54), (124), and (125) the density of eigenstates $\rho(\bar{\lambda})$ is obtained as

$$\begin{aligned} \rho(\bar{\lambda}) = \frac{1}{\pi}\int dx\, &[2(k_1ax^2 + k_3a)^{1/2}(k_2x^3 + k_4x)^{1/2} \\ &- k_2x^3 - k_1ax^2 - k_4x - k_3a + \bar{\lambda}]^{-1/2} \\ &\times [2(k_1ax^2 + k_3a)^{1/2}(k_2x^3 + k_4x)^{1/2} \\ &+ k_2x^3 + k_1ax^2 + k_4x + k_3a - \bar{\lambda}]^{-1/2} \end{aligned} \quad (129)$$

In case (iii) the relaxation times of the unstable and metastable states are obtained from Eqs. (92), (97), and (128),

$$\tau_u = \frac{1}{k_2(x_e - x_u)(x_u - x_m)} \tag{130}$$

$$\tau_m = \frac{k_2}{\pi} \frac{x_u^{1/2} x_m^{1/4} (x_e - x_u)^{3/4} (x_u^2 - x_m^2)^{3/4} (x_e - x_m)^{1/2}}{x_e^{3/4} (x_e + x_u)^{1/4} (x_e + x_m)^{1/2}} e^{\Omega \Delta_m} \tag{131}$$

where Δ_m is given by Eqs. (83) and (121).

The two different kinds of nonlinear birth and death processes discussed above show the wide applicability of the present theory. If the free-energy-like function $\phi_e(x)$ exists for the process, long-time behavior such as a critical slowing down and relaxations of metastable and unstable states can be obtained by our theory. Nonexponential decay of the critical slowing down corresponds to the anomalous accumulation of the lower lying eigenvalues. The relaxation time of the unstable state is finite, i.e., independent of Ω. It takes a very long time, of $O(e^{\Omega \Delta_m})$, for the metastable state to relax to the equilibrium state, where Δ_m is the free energy barrier of the metastable state and is given by Eq. (83).

7. CONCLUDING REMARKS

We have considered nonlinear stationary birth and death processes with one variable. Model systems described by such processes have been shown to yield information about relaxation and fluctuation phenomena of macrosystems. The eigenmodes and the eigenvalues of the master equation have been obtained through the use of a WKB approximation. The long-time relaxations were studied via the lower lying eigenmodes which are located at each of the extrema of the free-energy-like function. The one-variable case has now been essentially completely solved in this and a preceding work. Many additional interesting phenomena appear in the case of open, multivariable systems. These nonlinear multivariable systems cannot be analyzed by the method used in this paper because of the lack of a theory for the WKB approximation for equations with many variables. For such systems we still do not know how to treat the long-time relaxations.

APPENDIX

In this appendix we give the explicit expression for $\phi_e(x)$ and for the symmetrized master equation of an arbitrary birth and death process. These expressions will be limited, for the reasons given in the body of the paper, to the case of a one-variable system with one-step transitions.

The master equation for such a process is given by

$$\frac{\partial}{\partial t}P(n, t) = -[B(n) + D(n)]P(n, t) + B(n-1)P(n-1, t) + D(n+1)P(n+1, t) \tag{A.1}$$

where $B(n)$ and $D(n)$ denote the birth and death rates, respectively, and $n = 0, 1, 2, \ldots, N$. Both transition probabilities are assumed to satisfy Eq. (2). The equilibrium probability distribution $P_e(n)$ can be obtained from (A.1) as

$$P_e(n) = C\prod_{k=0}^{n-1} B(k) \prod_{l=n+1}^{N} D(l) \qquad \text{for } 1 \leqslant n \leqslant N-1 \tag{A.2}$$

$$P_e(0) = C\prod_{k=0}^{N-1} B(k), \qquad P_e(N) = C\prod_{l=1}^{N} D(l) \tag{A.3}$$

where

$$C^{-1} = \prod_{l=1}^{N} D(l) + \prod_{k=0}^{N-1} B(k) + \sum_{n=1}^{N-1} \prod_{k=0}^{n-1} B(k) \prod_{l=n+1}^{N} D(l) \tag{A.4}$$

The free-energy-like function can be expressed as

$$\Phi_e(n) = \text{const} + \sum_{k=0}^{n-1} \ln B(k) + \sum_{l=n+1}^{N} \ln D(l) \tag{A.5}$$

$$\phi_e(x) = \text{const} + \int_0^x dx' \ln b(x') + \int_x^1 dx' \ln d(x') \tag{A.6}$$

where $x = n/N$, $b(x) = (1/N)B(n)$, and $d(x) = (1/N)D(n)$.

Using $P_e(n)$, we can transform $P(n, t)$ into $\psi(n, t)$ by Eq. (8), and obtain the symmetrized master equation

$$(\partial/\partial t)\psi(n, t) = -[B(n) + D(n)]\psi(n, t) + [B(n-1)D(n)]^{1/2}\psi(n-1, t) + [B(n)D(n+1)]^{1/2}\psi(n+1, t) \tag{A.7}$$

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