Eigenvalue Problem of Metastability in Macrosystem

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Stochastic master equation is transformed into a self-adjoint form by using the detailed balance condition. A Fokker-Planck equation becomes formally equivalent to a Schrödinger equation by this transformation, where the inverse of a system-size parameter corresponds to Planck’s constant. For example, the decay process of a metastable state can be considered as an eigenvalue problem of multi-well potential in quantum mechanics. The decay rate corresponds to the first excited eigenvalue which almost degenerates with that of the ground state, i.e., the true equilibrium state. Calculations include the dependence on the system-size and external field. The process of approach to equilibrium distribution is analogous to the penetration or tunneling of wave-function in quantum mechanics.

§ 1. Introduction

We often find the examples of bi-stable or multi-stable problems in macrosystems, e.g., in the usual phase-transition, in the non-linear chemical reaction, in the laser system and in many other co-operative systems. The decay process of the metastable and unstable state cannot be dealt with in the linear theory of local stability, e.g., the decay rate cannot be determined by the local nature of the system.

Kubo et al. and Kitahara have presented new systematic methods to treat the stochastic macro-system, i.e., the system-size expansion and the Hamilton-Jacobi approximation for master equation. Though these can be said, in one sense, to include non-linear effects of fluctuation, they reveal apparent difficulty if applied to the multi-stable problems. One cannot approach the true equilibrium distribution starting from a localized distribution at the metastable or unstable point.

In these non-linear problems, we need the global stability of the system instead of the local one. The purpose of this paper is to investigate the stochastic relaxation process in such systems as an eigenvalue problem of the corresponding Fokker-Planck equation. The formal analogy between the stochastic process and quantum mechanics is successfully accepted in this problem.

In the next section (§ 2), a brief review on the self-adjoint transformation of master equation is given with relation to the detailed balance condition. The eigenvalue problem of the master equation will be simplified by this transformation. In § 3 we show the simple examples of the eigenvalue problem for the global stability of the Fokker-Planck equations using the equivalent Schrödinger equations. The accumulation of the eigenvalues, i.e., the decay rates in the marginal and
critical systems\textsuperscript{9} is easily obtained in this Schrödinger form. In § 4 the eigenvalues for a simplified bi-stable system are calculated and the relaxation process of the metastable state is discussed with the use of the low-lying eigenvalues and eigenfunctions. Present procedure is not so advantageous for the discussion of the relaxation process of the unstable state. A qualitative discussion on this problem is given in § 5 using the quantum mechanical terminologies.

§ 2. Self-adjoint form of master equation

Let \( x = \{x_i\} \) be stochastic variables which obey the Markovian master equation

\[
\frac{\partial}{\partial t} P(x, t) = -\mathcal{L}[x] P(x, t),
\]  
(2.1)

where \( P(x, t) \) is the probability distribution function and \( \mathcal{L}[x] \) is the Markovian evolution operator. An example of \( \mathcal{L}[x] \) is the Kramers-Moyal expansion which includes the differentiation with respect to \( x \). Here the master equation (2.1) is assumed to have the following properties:

(i) There exists an equilibrium distribution \( P_0(x) \) which is a unique asymptotic solution.

(ii) Detailed balance condition is fulfilled in the equilibrium state \( P_0(x) \).

One can transform the master equation (2.1) into a self-adjoint or an Hermite form on the basis of these assumptions. Put

\[
\Phi(x, t) = P_0(x)^{1/2} \psi(x, t)
\]  
(2.2)

and

\[
\mathcal{H}[x] = P_0(x)^{-1/2} \mathcal{L}[x] P_0(x)^{1/2},
\]  
(2.3)

then Eq. (2.1) is rewritten as

\[
\frac{\partial}{\partial t} \psi(x, t) = -\mathcal{H}[x] \psi(x, t).
\]  
(2.4)

Using the detailed balance condition (see Appendix A)

\[
\mathcal{L}^*[x] = P_0(x) \mathcal{L}^+[x] P_0(x)^{-1} = \mathcal{L}[x],
\]  
(2.5)

the transformed Markovian operator \( \mathcal{H}[x] \) is shown to be self-adjoint or Hermitian, i.e.,

\[
\mathcal{H}^+[x] = \mathcal{H}[x],
\]

where the adjoint operator is defined by

\[
\int_{-\infty}^{\infty} f(\mathcal{L} g) dx = \int_{-\infty}^{\infty} g(\mathcal{L}^+ f) dx.
\]  
(2.6)

As a simple example of the above procedure, a Fokker-Planck equation of one degree of freedom
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\[
\frac{\partial}{\partial t} P(x, t) = \left[ -\frac{\partial}{\partial x} c_1(x) + \frac{\varepsilon}{2} \frac{\partial^2}{\partial x^2} c_1(x) \right] P(x, t) \tag{2.7}
\]

is transformed into

\[
-\varepsilon \frac{\partial}{\partial t} \psi(x, t) = \left[ -\frac{\varepsilon^2}{2} \frac{\partial}{\partial x} c_1(x) \frac{\partial}{\partial x} + V(x) \right] \psi(x, t), \tag{2.8}
\]

where

\[
V(x) = \frac{1}{2c_1(x)} \left[ c_1(x) - \frac{\varepsilon}{2} c_1'(x) \right]^2 + \frac{\varepsilon}{2} \left[ c_1(x) - \frac{\varepsilon}{2} c_1'(x) \right]', \tag{2.9}
\]

and the equilibrium distribution is given by

\[
P_s(x) \propto \exp \left\{ \frac{2}{\varepsilon} \int_0^x \frac{c_1(s) - (\varepsilon/2) c_2'(s)}{c_1(s)} ds \right\}.
\]

Here \(\varepsilon\) is an arbitrary parameter, which is taken as the inverse of the system-size parameter \(\Omega\) in the following sections. It should be noted that Eq. (2.8) is the Schrödinger equation\(^b\) for a particle in one-dimensional potential \(V(x)\) except for the imaginary time and space-dependent mass \(1/c_1(x)\), and the smallness parameter \(\varepsilon\) corresponds to Planck's constant \(\hbar\).

**§ 3. Eigenvalue problem of the Fokker-Planck equation**

Hereafter we take the second moment in Eq. (2.7) as \(c_2(x) = 2s\) and \(\varepsilon\) as the inverse of the system-size parameter \(\Omega\), then the transformed equation (2.8) simply becomes

\[
\varepsilon \frac{\partial}{\partial t} \psi(x, t) = \mathcal{H}[x] \psi(x, t), \tag{3.1}
\]

\[
\mathcal{H}[x] = -\varepsilon^2 \frac{\partial^2}{\partial x^2} + V(x), \quad V(x) = \left( \frac{F'(x)}{2} \right)^2 - \frac{\varepsilon}{2} F''(x), \tag{3.2}
\]

where \(F(x)\) is defined by

\[
F(x) = -\varepsilon \ln P_0(x) = -\int_0^x c_1(s) ds, \tag{3.3}
\]

which is called free-energy hereafter for simplicity. The potential \(V(x)\) in this Schrödinger equation (3.2) has the following properties:

(i) \(V(x) < 0\) at the minimum of \(F(x)\) (i.e., \(F'(x) = 0, F''(x) > 0\)),

(ii) \(V(x) > 0\) in the spinodal region where \(F''(x) \leq 0\),

(iii) \(\lim_{x \to \pm \infty} V(x) = +\infty\) in almost every case,

and approximately:

\(^b\) A transformation (e.g., \(dx' = \sqrt{2/c_1(x)} dx\) and \(P(x, t) dx = Q(x', t) dx'\)) makes it possible to assume this form generally.
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Fig. 1. Simple examples for $F(x)$ vs. $V(x)$ correspondence. Broken lines in $V(x)$ denote
the eigenvalue levels $\{\epsilon_n\}$ which are calculated exactly for (a) and (b), and by the
WKB approximations for (c) and (d) except for $\epsilon_{n_0}=0$ in (d).

(iv) Minimum points of $V(x)$ correspond to extremum (minimum or max­
imum) of $F(x)$,
(v) Maximum points of $V(x)$ correspond to the spinodal points $F''(x)=0$,
i.e., the inflection points,
for sufficiently small $\varepsilon$.

Examples of the correspondence $F(x)$ vs. $V(x)$ are shown in Fig. 1.

If one puts

$$\psi(x, t) = e^{-it}\phi(x), \quad (3.4)$$

the eigenvalue equation for Eq. (3.1) is given by

$$\epsilon \phi(x) = \mathcal{H}[x] \phi(x). \quad (3.5)$$

The eigenvalues are all real because of the Hermiteness of $\mathcal{H}[x]$. When the
steady distribution $P_0(x)$ is stable, or normalizable, i.e.,

$$\int_{-\infty}^{\infty} dx \exp \{-F(x)/\varepsilon\} = \text{finite}, \quad (3.6)$$

Eq. (3.5) has the trivial ground state solution

$$\lambda_0=0 \quad \text{and} \quad \phi_0(x) = P_0(x)^{1/2} \exp \{-F(x)/2\varepsilon\}, \quad (3.7)$$

and the other eigenvalues are all positive. On the other hand, one finds that

$$\lambda_n>0$$

for unstable examples (b) and (c) in Fig. 1. This is because these two examples
have no stable steady-solution or Eq. (3.6) is not fulfilled.

The eigenvalues for the examples (a) ~ (d) in Fig. 1 are easily obtained as follows:
An = nγ, \quad (n = 0, 1, 2, \cdots) \quad (3.8)

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\begin{align}
\lambda_n &= (n + 1) |\gamma|, \quad (n = 0, 1, 2, \cdots) \quad (3.9)
\end{align}

(c) $F(x) = -\frac{T}{3}x^3, \quad (\gamma > 0) \quad V(x) = \frac{T}{3}x^4 + 2\varepsilon \gamma x$, \quad (marginal)

\begin{align}
\lambda_0 > 0, \quad \lambda_n &= \left(n + \frac{1}{2}\right)^{\frac{4}{3}} \gamma^{2/3} 4A_k^{2/3},
\end{align}

(d) $F(x) = \frac{T}{4}x^4, \quad (\gamma > 0) \quad V(x) = \frac{T}{4}x^6 - 3\varepsilon \gamma x^4$, \quad (critical)

\begin{align}
\lambda_0 = 0, \quad \lambda_n &= \left(n + \frac{1}{2}\right)^{\frac{3}{2}} \gamma^{1/2} 4A_k^{1/2},
\end{align}

where

\begin{align}
A_k = \frac{1}{\pi} \int_0^1 \sqrt{1-x^2} \, dx = \frac{1}{2\pi^2} B\left(1, \frac{3}{2}\right)
\end{align}

and the $\lambda_n$'s for (c) and (d) are obtained by the WKB approximation neglecting the $\varepsilon$-terms in the respective potentials. There occurs the accumulations of eigenvalues for small $\varepsilon$ in the marginal (c) and critical (d) examples. Actually it can be shown that the eigenvalues are exactly scaled as

\begin{align}
\lambda_n (\varepsilon) = \varepsilon^{1/3} (k + 1) \lambda_n (1)
\end{align}

for the free energy

\begin{align}
F(x) = \frac{T}{k+1}x^{k+1}. \quad (k = 1, 2, 3, \cdots)
\end{align}

The same results are already given by Kubo et al.\textsuperscript{11}

Hereafter we restrict the problem to stable cases where we can expect that

\begin{align}
\lambda_0 = 0, \quad \phi_0 (x) = P_0 (x)^{1/2} \quad \text{and} \quad \lambda_n > 0 \quad \text{for} \ n \geq 1
\end{align}

and define the ortho-normal set $\{\lambda_n, \phi_n (x)\}$ of eigenvalues and eigenfunctions of $\mathcal{H} [x]$. The wave function in Eq. (3.1) and probability distribution function can be expanded as

\begin{align}
\phi (x, t) = \sum_{n=0}^{\infty} a_n e^{-\lambda_n t} \phi_n (x)
\end{align}

and

\begin{align}
P(x, t) = \sum_{n=0}^{\infty} a_n e^{-\lambda_n t} \phi_n (x) \phi_n (x),
\end{align}
where

\[ a_n = \int_{-\infty}^{\infty} \phi_n(x) \phi(x, 0) \, dx , \quad (3\cdot18) \]

and \( a_0 = 1 \) because of the normalization condition of \( P(x, 0) \).

§ 4. The decay process of metastable state

Let us consider the bi-stable system of one degree of freedom. The corresponding Schrödinger equation is that for a particle in a triple-well as is shown in Fig. 2. Two barriers, which may be called spinodal barriers, separate these three wells. One may take the free energy as

\[ F(x) = \frac{1}{4} x^4 - \frac{1}{2} a^2 x^2 - H x , \quad (4\cdot1) \]

which has two minimum points at \( x = \pm a \) for the external field

\[ |H| < H_s = 2a^3/3\sqrt{3} . \]

The detailed form is not so essential in the following discussion if the parameter \( \varepsilon \) is sufficiently small. For the kinetic Weiss-Ising model, the free energy may be alternatively chosen as

\[ F(x) = \frac{1}{2} \left\{ (1+x) \ln(1+x) + (1-x) \ln(1-x) \right\} - \frac{\beta}{2} x^2 - \beta H x . \]

The necessary quantities are \( F(x) \) and \( F''(x) \) at \( x = \alpha, \beta, \gamma \).  (See Fig. 2.)

Take the metastable initial state to be left-half part of the equilibrium distribution

\[ P(x, 0) = P_0(x) \theta(\gamma - x) / W(\infty) \quad (4\cdot2) \]

and

\[ \psi(x, 0) = \phi_0(x) \theta(\gamma - x) / W(\infty) , \quad (4\cdot3) \]

where

\[ W(\infty) = \int_{-\infty}^{\infty} P_0(x) \, dx \quad (4\cdot4) \]

and
\[ \theta(x) = \begin{cases} 1 & \text{for } x \geq 0, \\ 0 & \text{for } x < 0. \end{cases} \]

Then the expansion coefficients \((3 \cdot 18)\) are given by

\[ a_n = \frac{1}{W(\infty)} \int_{-\infty}^{\infty} \phi_n(x) \phi_n(x) \theta(x-x) \, dx. \]  

(4.5)

One may define the measure of the decay process by

\[ W(t) = \int_{-\infty}^{\infty} P(x,t) \, dx. \]  

(4.6)

With the use of Eqs. \((3 \cdot 17), (4 \cdot 4)\) and \((4 \cdot 5)\) this quantity is calculated as

\[ W(t) = W(\infty) \{1 + \sum_{n=1}^{\infty} a_n e^{-\lambda_n t}\}, \]

(4.7)

which relaxes from unity to \(W(\infty)\).

The above discussion is general. If the central barrier of the free energy is sufficiently high, the discussion can be more simplified: In this case energy levels or decay constants \(\{\lambda_n\}\) can be expected to be

\[ \lambda_0 \gg \lambda_i = \lambda_0 (= 0), \]

(4.8)

that is, the first excited level almost degenerates with the ground state level. Then the final stage of the decay process is well approximated by

\[ \psi(x,t) \cong \phi_0 + a_i \phi_i e^{-\lambda_i t}, \]  

(4.9)

\[ P(x,t) \cong P_0(x) + a_i \phi_i e^{-\lambda_i t} \]  

(4.10)

and

\[ W(t) \cong W(\infty) \{1 + a_i e^{-\lambda_i t}\}. \]  

(4.11)

In this case the first excited level \(\lambda_i\) can be taken as the decay rate of metastable state, and the metastable wave function is constructed as \(\phi_0 + a_i \phi_i\). This can be understood simply for the symmetric case \(H=0\): The wave functions of the ground and first excited states are approximated by

\[ \phi_0(x) \equiv (\psi_L(x) + \psi_R(x))/\sqrt{2} \quad \text{(symmetric)} \]

and

\[ \phi_1(x) \equiv (\psi_L(x) - \psi_R(x))/\sqrt{2} \quad \text{(anti-symmetric)} \]  

(4.12)

where \(\psi_R(x)\) and \(\psi_L(x)\) are localized ground states in the right and left wells in the potential \(V(x)\) respectively, and \(\psi_L(x) = \psi_R(-x)\) in this symmetric case. (See Fig. 3) Then the initial, metastable wave function can be constructed as

\[ \psi(x,0) = \phi_0 + \phi_1 = \sqrt{2} \psi_L(x). \]  

(4.13)

The level splitting \(\lambda_i - \lambda_0\) can be calculated with the use of quasi-classical
methods. The details are given in Appendix B. Putting $\lambda_0=0$, the decay rate $\lambda_i$ is given by

$$\lambda_i = \frac{1}{4\sqrt{\pi}} \sqrt{|F''(\gamma)|} e^{-F(\gamma)/2} \left\{ \sqrt{F''(\alpha)} e^{F(\alpha)/2} + \sqrt{F''(\beta)} e^{F(\beta)/2} \right\}, \quad (4.14)$$

where $\alpha$, $\beta$ and $\gamma$ are the extremum points of $F(x)$ in Fig. 2. In the symmetric case ($H=0$)

$$\lambda_1(0) = \frac{1}{2\sqrt{\pi}} \sqrt{F''(0)} e^{-\Delta_0/2}, \quad (4.15)$$

where $\alpha=-a$, $\beta=a$, $\gamma=0$ and

$$\Delta_0 = F(0) - F(\pm a).$$

For the small external field

$$a H \ll \varepsilon,$$

Eq. (4.14) is approximated by

$$\lambda_i(H) \approx \left\{ 1 + \frac{1}{2} \left( \frac{aH}{\varepsilon} \right)^2 \right\} \lambda_i(0), \quad (4.16)$$

and for the case $a^{-1} \varepsilon \ll H \ll H_c$,

$$\lambda_i(H) \approx \frac{1}{4\sqrt{\pi}} \sqrt{F''(\alpha)} |F''(\gamma)| e^{-\Delta_0/2}$$

$$\approx \frac{1}{\varepsilon} e^{aH/\varepsilon} \lambda_i(0), \quad (4.17)$$
where
\[ J = F(\gamma) - F(\alpha). \]

The result (4·16) can be also obtained by perturbational method, and Eq. (4·17) agrees with the early work of Kramers and the recent Langer's except for the constant factor. The same results including the system-size dependence are given by Griffiths et al. and Saito. The field dependence of Eq. (4·14) is compared with the direct, numerical calculation of the original Fokker-Planck equation. The numerical decay rate is determined by assuming Eq. (4·11), and the result is shown in Fig. 4. The ratio of both results at \( H=0 \) is given by
\[ \frac{\lambda_1(0) \text{ numerical}}{\lambda_1(0) \text{ predicted}} \approx 1.017 \sim 1.020. \]

The calculation of the eigenvalues of higher levels is difficult in general. The second excited level \( \lambda_2 \) is roughly estimated as
\[ \varepsilon \lambda_2 \approx \varepsilon F''(a) \text{ or } \varepsilon |F''(0)|, \quad (4·18) \]
where \( \varepsilon F''(a) \) is the localized, first excited level in the well located at \( x=a \), and \( \varepsilon |F''(0)| \) the ground state level at \( x=0 \), respectively. In any case we can surely expect that \( \lambda_2 \) is of order unity from (4·18), then the assumption (4·8) is fulfilled in the case of small \( \varepsilon \).

Summary of this section is as follows:

The decay process of the metastable
state is that, the first stage is the relaxation to a metastable distribution, the second stage is the penetration of the probability distribution function (or wave function) through the free-energy barrier, and the time scales of two processes are well separated in the macro-system. Numerical calculations clarify this penetration process as is shown in Fig. 5.

§ 5. The decay process of unstable state

Another difficult problem in the bi-stable system is the decay process of the distribution function initially located just on the unstable point, i.e., the central top of the free energy in Fig. 2. Recently, Suzuki has presented a scaling theory on this problem. The essence of it is the smooth continuation of two regimes, i.e., the initial, linear regime and the drift regime where the distribution function is broadened with the variance of order unity. A brief picture is given in the following within our Schrödinger scheme. The free energy is assumed to be symmetric for simplicity, i.e., $H=0$ in Eq. (4·1).

(i) initial stage—diffusion process of wave function

Starting from the $\delta$-function at $x=0$, the first stage of the wave equation (3·1) is mainly the diffusion process, the wave function approaching the local ground state $\psi_c(x)$ in the central well in $V(x)$. The order of time-scale of this process is estimated as $-\log \varepsilon$ by the Gaussian approximation.

(ii) second stage—penetration through the spinodal barriers

The broadened wave function penetrates through the spinodal barriers, i.e., decomposes into two peaks in the stable wells at $x=\pm a$. One may find the wave function of the second or third state to be

$$\phi_i \equiv \phi_t \text{ and } \lambda_i \equiv |F''(0)|, \quad (i=2 \text{ or } 3, \cdots)$$

In the case $|F''(0)| \ll F''(a)$, it can be surely supposed that

$$\phi_2 \equiv u \psi_c - \nu (\psi_L + \psi_R)/\sqrt{2}, \quad (u^2 + \nu^2 = 1)$$

as is shown in Fig. 3. Then taking the initial wave function of this stage at $t=t_0$ as

$$\phi(x, t_0) = \phi_0 + \frac{1}{v} \phi_2 \approx \frac{u}{v} \psi_c,$$

the decomposition process is expressed by

$$\phi(x, t) \approx \phi_0 + \frac{1}{v} \phi_2 e^{-\lambda_t(t-t_0)},$$

the decomposing rate being $\lambda_0 \sim O(1)$. This can be said in other words as follows: For the broadened wave function the diffusion process can be neglected and the wave equation (3·1) is approximated by

$$\varepsilon \frac{\partial \psi}{\partial t} = -V(x)\psi,$$
then the wave function mainly decays in the region $V(x) > 0$ and grows in the region $V(x) < 0$. This cannot be applied to the distribution function itself, but it suggests qualitative aspects that the decomposed peaks grow markedly out of the spinodal region. This can be directly ascertained by the numerical calculations of the Fokker-Planck equation as is shown in Fig. 6.

Fig. 6. Calculated decay process of the distribution function $P(x, t)$ from a Gaussian at the unstable point $x=0$ in (a), and the wave function $\psi(x, t)$ in (b). $F(x)$ is given by Eq. (4·1) with $a=1$ and $H=0$, and $\varepsilon$ is taken to be $1/40$. In both figures only the right-half parts are drawn because of the symmetry.

§ 6. Summary and discussion

The Hermiteness of master equation is directly connected with the detailed balance as is briefly summarized in Appendix A. Recently Hasegawa has discussed the same problem. It can be said as a conclusion that the eigenvalues of master equation are all real if the detailed balance condition is fulfilled, at least in the case where included variables are all $\alpha$-variables, i.e., symmetric under the time-reversal transformation. Contrary to this, the cyclic balance situation is characterized by complex eigenvalues of master equation.

The self-adjoint form of master equation has been used by Ruijgrok and Tjon for the kinetic Weiss-Ising model, and Kawasaki has used the second quantization technique in the Schrödinger equation (2·8) for many degrees of freedom in his application of mode-coupling theory to the nonequilibrium systems.

The Fokker-Planck equation used in § 3 is too simplified to investigate the actual macro-system. Applications seem to be restricted to a few problems, e.g., the kinetic Weiss-Ising model, a stochastic model for the homogeneous nucleation, and others which can be described by a single variable. Critical phenomena is an example for which one needs more complicated descriptions. Kawasaki has used the field-theoretical technique in the nucleation problem. The simplified method of this paper, however, gives us a clear, rigorous picture of the essence of the decay process of a metastable state in the macroscopic system.

The decay rate of a metastable state has been calculated by several authors from different points of view. The difference of the constant factor
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may be caused by the difference of the methods. Our results of the eigenvalue method agree with the numerical results within a few percent errors. Small discrepancy for large $H$ in Fig. 4 should be due to the limitation of the computation, i.e., due to the large values of $\varepsilon$ and $H$. It should be noted that in a macro-system ($\varepsilon \ll 1$), the relaxation rate is largely enhanced by a factor $\exp(a|H|/\varepsilon)$ for a small, but finite field $H$, compared with the case $H=0$, i.e., the co-existing state.

Discussion on the relaxation from the unstable state is not so rigorous compared with the metastable case. But the qualitative discussion in § 5 is quite general, i.e., independent of the details of the free-energy. A typical example for it is the following model which is very similar to Eq. (4.1) with $H=0$:

$$F(x) = \begin{cases} 
(x+a)^2/2 - a^2/4 & \text{for } x<-a/2, \\
-x^2/2 & \text{for } |x|\leq a/2, \\
(x-a)^2/2 - a^2/4 & \text{for } x>a/2.
\end{cases}$$

It can be shown for this model that the decomposed peaks begin to appear at the spinodal point $x = \pm a/2$, using Suzuki's idea.

It is concluded that the equation of the most probable path loses its meaning in such problems as the relaxations of metastable and unstable states in the multi-stable systems. Clearly the decay process of metastable state is a kind of penetration phenomena, by which a new peak of distribution function begins to grow in the lowest bottom of the free energy.

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Appendix A

Time-reversed master equation and detailed balance

Let $P(x, t|x_0, t_0)$, where $t \geq t_0$, be the conditional distribution function with the condition $x=x_0$ at $t=t_0$, which obeys

$$\frac{\partial}{\partial t} P(x, t|x_0, t_0) = -\mathcal{L}[x] P(x, t|x_0, t_0). \quad (A\cdot1)$$

Using the Chapman-Kolmogorov equation

$$P(x, t|x_0, t_1) = \int dx_0 P(x, t|x_0, t_0) P(x_0, t_0|x_1, t_1), \quad (t \geq t \geq t_1) \quad (A\cdot2)$$

another evolution equation, i.e., Kolmogorov's backward equation

$$\frac{\partial}{\partial t_0} P(x, t|x_0, t_0) = \mathcal{L}^+[x_0] P(x, t|x_0, t_0) \quad (A\cdot3)$$
can be obtained, where $\mathcal{L}^+[x]$ is defined by Eq. (2·6). For the discussion on
the time-reversal symmetry of master equation, one needs the forward and backward
equations for the joint probability

$$P_z(x_0, t_0; x, t) = P(x, t|x_0, t_0) P_0(x_0), \quad (t \geq t_0) \quad (A·4)$$

where the stationarity is assumed. The forward equation is just the same as
Eq. (A·1), i.e.,

$$\frac{\partial}{\partial t} P_z(x_0, t_0; x, t) = -\mathcal{L}^+[x] P_z(x_0, t_0; x, t). \quad (A·5)$$

The backward one is obtained by differentiating the identity (A·4) with respect
to $t_0$ and by using (A·3),

$$\frac{\partial}{\partial t_0} P(x_0, t_0; x, t) = P_0(x_0) \mathcal{L}^+[x] P(x, t|x_0, t_0)$$

$$= \mathcal{L}^*[x] P_z(x_0, t_0; x, t), \quad (A·6)$$

where

$$\mathcal{L}^*[x] = P_0(x) \mathcal{L}^+[x] P_0(x)^{-1}. \quad \text{(operator)} \quad (A·7)$$

The detailed balance or micro-reversibility condition

$$P_z(x_0, t_0; x, t) = P_z(x, t_0; x_0, t) \quad (A·8)$$

can be rewritten in operator form;

$$\mathcal{L}^*[x] = \mathcal{L}^+[x] \quad (A·9)$$

by the use of Eqs. (A·5~7). Here we have assumed that the variables $x = \{x_i\}$
are all $\alpha$-variables.

**Appendix B**

**Quasi-classical estimation for $\lambda_1 - \lambda_0$**

From the eigenvalue equations (3·5) for $n=0$ and 1, i.e.,

$$\varepsilon \lambda_0 \phi_0 = -\varepsilon \phi_0'' + V \phi_0$$

and

$$\varepsilon \lambda_1 \phi_1 = -\varepsilon \phi_1'' + V \phi_1, \quad (B·1)$$

an identity

$$(\lambda_1 - \lambda_0) \phi_0 \phi_1 = \varepsilon (\phi_0 \phi_1 - \phi_0 \phi_1')' \quad (B·2)$$

is obtained. Integrating Eq. (B·2) from $x = -\infty$ to $x = \gamma$, a formula for the level
splitting is given by

$$\lambda_1 - \lambda_0 = -\varepsilon \phi_0 (\gamma) \phi_1' (\gamma) \int_{-\infty}^{\gamma} \phi_0 \phi_1 dx, \quad (B·3)$$
where the condition
\[
\phi_0'(\gamma) = -\frac{F'(\gamma)}{2\varepsilon}\phi_0(\gamma) = 0 ,
\]  
(B·4)
is used. If the potential barrier is sufficiently high, or \(\varepsilon\) is small enough, we can construct \(\phi_0\) and \(\phi_1\) as follows:
\[
\phi_0 \equiv u\psi_L + v\psi_R
\]  
and
\[
\phi_1 \equiv v\psi_L - u\psi_R , \quad (u^2 + v^2 = 1) \quad (B·5)
\]where \(\psi_L\) and \(\psi_R\) are normalized wave functions of the localized ground states in the left \((x=\alpha)\) and right \((x=\beta)\) wells, respectively. Using Eq. (B·5), the denominator on the right-hand side of Eq. (B·3) is approximated by
\[
\int_{-\infty}^{\infty} \phi_0\phi_1 dx = uv \int_{-\infty}^{\infty} \psi_L^2 dx = uv . \quad (B·6)
The derivative of \(\phi_1\) at \(x=\gamma\) is necessary to complete the calculations. This can be obtained by the WKB approximations,
\[
\psi_L'(\gamma) \equiv -\frac{1}{\varepsilon} \sqrt{V(\gamma)} \psi_L(\gamma) = -\sqrt{|F''(\gamma)|/2\varepsilon} \psi_L(\gamma) \quad (B·7)
\]and
\[
\psi_R'(\gamma) \equiv \frac{1}{\varepsilon} \sqrt{V(\gamma)} \psi_R(\gamma) = \sqrt{|F''(\gamma)|/2\varepsilon} \psi_R(\gamma) . \quad (B·8)
\]By the condition (B·4) it is obtained that
\[
u\psi_L(\gamma) \equiv v\psi_R(\gamma) \quad \text{and} \quad \psi_L(\gamma) \equiv \phi_0(\gamma)/2u . \quad (B·9)
\]Using Eqs. (B·5~9) the level splitting is rewritten as
\[
\lambda_1 - \lambda_0 = \sqrt{\frac{\varepsilon}{2}} \int \frac{|F''(\gamma)|}{2} \phi_0(\gamma)^2 d\gamma . \quad (B·10)
\]The unknown quantities in Eq. (B·10) can be calculated by the WKB approximation, but here let us take another way. Remembering that \(\phi_i^*\) is the equilibrium distribution function \(P_0(x)\), i.e.,
\[
\phi_0^2(x) = N^{-1}\exp[-F(x)/\varepsilon] , \quad (B·11)
\]one obtains
\[
\phi_0(\gamma)^2 = N^{-1}\exp[-F(\gamma)/\varepsilon] , \quad (B·12)
\]where \(N\) is the normalization factor. Integrating \(\phi_0(x)^2\), one can evaluate \(u^2\) and \(v^2\) as follows:
\[
u^2 \equiv \int_{-\infty}^{\infty} \phi_0(x)^2 dx = N^{-1}\sqrt{2\pi\varepsilon/F''(\alpha)} \exp[-F(\alpha)/\varepsilon] \quad (B·13)
where the normalization factor $N$ is determined by the condition

$$u^2 + v^2 = 1.$$  

The final expression for the level splitting $\lambda_1 - \lambda_0$ is given by

$$\lambda_1 - \lambda_0 \simeq \frac{1}{4\sqrt{\pi}} \sqrt{|F'(\gamma)|} \exp[-F(\gamma)/\varepsilon] \times \{\sqrt{F''(\alpha)} \exp[F(\alpha)/\varepsilon] + \sqrt{F''(\beta)} \exp[F(\beta)/\varepsilon]\}.$$  

References

7) R. Fürth, Z. Phys. 81 (1933), 143.
   E. Nelson, Dynamic Theories of Brownian Motion, (Princeton Univ. 1967).
10) H. A. Kramers, Physica 7 (1940), 284.
16) See for example,