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Stochastic Theory of Nonlinear Rate Processes with Multiple Stationary States. II. Relaxation Time from a Metastable State

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We have developed a methodology for obtaining a Fokker–Planck equation for nonlinear systems with multiple stationary states that yields the correct system size dependence, i.e., exponential growth with system size of the relaxation time from a metastable state. We show that this relaxation time depends strongly on the barrier height $U(x)$ between the metastable and stable states of the system. For a Fokker–Planck (FP) equation to yield the correct result for the relaxation time from a metastable state, it is therefore essential that the free energy function $U(x)$ of the FP equation not only correctly locate the extrema of $U(x)$, but also have the correct magnitude U at these extrema. This is accomplished by so choosing the coefficients of the FP equation that its stationary solution is identical to that of the master equation that defines the nonlinear system.

KEY WORDS: Stochastic processes; nonlinear rate processes; Fokker–Planck equation; mean first passage times; metastable states; system size expansion.

1. INTRODUCTION

Fluctuation, rate, and relaxation phenomena in nonlinear multistate systems have recently attracted considerable attention.(1–12) The first attempts at the analysis of fluctuation and relaxation phenomena in nonlinear systems were based on a Fokker–Planck (FP) equation approach in parallel with its successful use in the theory of linear systems. Van Kampen(1) demonstrated, however, that in dealing with nonequilibrium processes in nonlinear macrosystems it is in general necessary to use a full master equation rather than the

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FP equations obtained from a master equation or from a Langevin-type equation. He used a birth and death process as a master equation model and formulated a system-size expansion method in which the small expansion parameter is the inverse of the system size. This approach has also been investigated and applied by other investigators(3) and has been shown to be a powerful method for the calculation of nonequilibrium properties of macrovariables in many nonlinear systems.

There are, however, cases in which the system-size expansion method is not applicable. In particular, it cannot be used in the analysis of the *long-time behavior* of nonlinear systems with multiple stationary states. Alternative approaches to this problem have been developed by various authors. Thus, the relaxation from a metastable state has been investigated by an extension of Kramers' method,(5,6,13) by a double Gaussian approximation method,(7,10) by a relaxation mode analysis,(8,12) and by a mean first passage time calculation.(9) The question that has been addressed in these analyses is that of the influence of the system size on the relaxation time of a system from a metastable state to the equilibrium state. All of these methods yield identical results for appropriately chosen models. It is now clear that the system size dependence of the relaxation time from a metastable state depends only on certain *gross* features of the models, so that quite different models corresponding to different physical problems will yield similar results.

In the preceding paper of this series, Oppenheim *et al.*(9) studied the system size dependence of the relaxation times of a nonlinear system via a master equation approach. This involves some rather cumbersome analysis. From some of our earlier work on linear stochastic systems,(14) it is clear that the simplest and most tractable method for the calculation of relaxation times is via the FP equation. As van Kampen(1) has shown, the *usual* FP equation approach yields incorrect results for nonlinear systems, a finding which we verify in this paper. However, as we will demonstrate below, it *is* possible to derive a FP equation using a well-defined and reasonable prescription that does yield the correct relaxation times. This finding opens up the use of the more convenient techniques of the FP equation for the discussion of relaxation times in nonlinear, multistate systems.

In Section 2 we derive various possible forms of FP equations for a particular nonlinear system with several stationary states. In Section 3 we obtain the equations for the mean first passage time for the generic FP equation. To estimate the relaxation time from the metastable state we use the mean first passage from this state to appropriately chosen boundary states. In Section 4 we explicitly calculate the system size dependence of the relaxation time from a metastable state and thereby establish the correct FP equation that must be used for such calculations. This FP equation is distinguished from the other FP equations discussed here by the property that its stationary solution is the correct equilibrium solution for the nonlinear system under study. This is the sufficient condition for the successful calculation of the relaxation time from a *metastable state.*

In a subsequent paper we will show that *all* the various FP equations discussed here yield identical and correct results for the system-size dependence of the relaxation times from *unstable states*. The reason for this dichotomy is discussed briefly in Section 4.

2. CHOICES OF FOKKER-PLANCK EQUATIONS

A Fokker-Planck equation has the general form

$$\frac{\partial}{\partial t} P(x, t) = -\frac{\partial}{\partial x} [A(x)P(x, t)] + \frac{\epsilon}{2} \frac{\partial^2}{\partial x^2} [B(x)P(x, t)] \tag{1}$$

where $P(x, t)$ is the time-dependent probability distribution of an intensive macroscopic variable x, and ϵ is the inverse of the system size V, i.e., $\epsilon = V^{-1}$. The coefficients $A(x)$ and $B(x)$ depend on the particular system under study. The stationary distribution of Eq. (1), i.e., the solution of (1) with the left-hand side equal to zero, is denoted by $P_{st}(x)$ and is given by

$$P_{st}(x) = \frac{K}{B(x)} \exp\left[-\frac{1}{\epsilon} U(x)\right] \tag{2}$$

where K is a normalization constant and

$$U(x) = -2 \int^{x} \frac{A(x')}{B(x')} dx' \tag{3}$$

The quantity U can be considered a dimensionless free energy. In a thermal environment, $U = U^*/kT$, where U^* then has the dimension of energy per unit volume.

In this section we discuss the different FP equations that can be derived by various standard methods. For specificity in the calculation of the relaxation time from a metastable state, we choose the nonlinear chemical reaction system studied previously by Oppenheim *et al.*,(9) i.e.,

$$\mathrm{A} \underset{k_{-1}}{\overset{k_1}{\rightleftarrows}} \mathrm{X}, \qquad \mathrm{A} + \mathrm{X} \underset{k_{-2}}{\overset{k_2}{\rightleftarrows}} 2\mathrm{X}, \qquad \mathrm{A} + 2\mathrm{X} \underset{k_{-3}}{\overset{k_3}{\rightleftarrows}} 3\mathrm{X} \tag{4}$$

Here the macrovariable of interest is the time-dependent number density $x(t)$ of species X, while the number of molecules of species A is assumed to be constant in time. The deterministic rate equation for the number $N_x(t)$ of molecules X at time t is, with V equal to the volume of the reaction systems,

$$\dot{N}_x(t) = k_1 A + \left(\frac{k_2}{V} A - k_{-1}\right) N_x(t) + \left(\frac{k_3}{V^2} A - \frac{k_{-2}}{V}\right) N_x^2(t) - \frac{k_{-3}}{V^2} N_x^3(t) \tag{5}$$

This rate equation can be rewritten as

$$\dot{x}(t) = \kappa[\alpha - x(t)][\beta - x(t)][\gamma - x(t)] \tag{6}$$

where $x(t) = N_x(t)/V$ is the number density of species X and where κ, α, β, and γ are constants whose relation to the rate coefficients and system size can be obtained from Eq. (5). From (6) we see that this system has up to three stationary states given by $x = \alpha$, $x = \beta$, and $x = \gamma$.

We will construct three different FP equations to describe the system (4). Their origin is schematically indicated in Fig. 1. The first FP equation of Fig. 1 is obtained by converting the deterministic rate equation (6) into a Langevin equation through the addition of a random noise term $R(t)$:

$$\dot{x}(t) = \kappa[\alpha - x(t)][\beta - x(t)][\gamma - x(t)] + R(t) \tag{7}$$

The random noise models the microscopic fluctuations of the system. We assume that $R(t)$ is Gaussian and δ-correlated with zero mean and variance of order ϵ with $\epsilon = V^{-1}$, i.e.,

$$\langle R(t)\rangle = 0, \qquad \langle R(t)R(t')\rangle = C\kappa\epsilon\, \delta(t - t') \tag{8}$$

where C is a constant independent of ϵ. By standard methods, the Langevin equation (7) can be converted to the FP equation (1) with coefficients

$$A_1(x) = \kappa(\alpha - x)(\beta - x)(\gamma - x), \qquad B_1(x) = 2C\kappa \tag{9}$$

To obtain the second FP equation of Fig. 1 we first model the system (4) by a birth and death type master equation according to standard procedures. The master equation for the probability distribution $P(x, t)$ is given by$^{(9)}$

$$\begin{aligned}\partial P(x, t)/\partial t = {} & \mathscr{A}(x, 1)P(x - \epsilon, t) + \mathscr{A}(x, -1)P(x + \epsilon, t) \\ & - [\mathscr{A}(x, 1) + \mathscr{A}(x, -1)]P(x, t)\end{aligned} \tag{10}$$

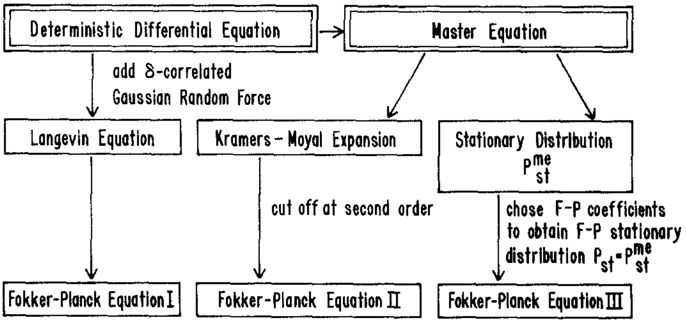

Fig. 1. Flowsheet for the derivation of the Fokker–Planck equations.

The normalized transition rates $\mathscr{A}(x, \pm 1)$ are

$$\begin{aligned} \mathscr{A}(x, 1) &= \kappa[(\alpha + \beta + \gamma)x^2 + \alpha\beta\gamma] + O(\epsilon) \\ \mathscr{A}(x, -1) &= \kappa x(x^2 + \alpha\beta + \beta\gamma + \gamma\alpha) + O(\epsilon) \end{aligned} \tag{11}$$

Performing a Kramers–Moyal expansion of (10) and retaining only the first and second moments of the transition probabilities leads to the FP equation (1) with coefficients

$$A_2(x) = \kappa(\alpha - x)(\beta - x)(\gamma - x), \qquad B_2(x) = \kappa(\alpha + x)(\beta + x)(\gamma + x) \tag{12}$$

Note that the FP equation obtained here is quite different from the one obtained via the Langevin equation.

The third FP equation in Fig. 1 involves the exact stationary distribution of the master equation (10), which is obtained by setting the left-hand side equal to zero. We write this stationary solution in the form

$$P_{\mathrm{st}}^{\mathrm{ME}}(x) = f(x) \exp[-(1/\epsilon)\phi_e(x)] \tag{13}$$

where[8] $f(x)$ is of $O(\epsilon^0)$ and

$$-\frac{d}{dx}\phi_e(x) = \ln \frac{\mathscr{A}(x, 1)}{\mathscr{A}(x, -1)} \tag{14}$$

From Eqs. (10) and (11) it follows that

$$\begin{aligned} \phi_e(x) = \text{const} &- x \ln \frac{(\alpha + \beta + \gamma)x^2 + \alpha\beta\gamma}{(x^2 + \alpha\beta + \beta\gamma + \gamma\alpha)x} \\ &- x - 2\left(\frac{\alpha\beta\gamma}{\alpha + \beta + \gamma}\right)^{1/2} \tan^{-1}\left[\left(\frac{\alpha + \beta + \gamma}{\alpha\beta\gamma}\right)^{1/2} x\right] \\ &+ 2(\alpha\beta + \beta\gamma + \gamma\alpha)^{1/2} \tan^{-1}[(\alpha\beta + \beta\gamma + \gamma\alpha)^{-1/2} x] \end{aligned} \tag{15}$$

The FP equation is then constructed in such a way that its stationary solution $P_{\mathrm{st}}(x)$ [cf. Eq. (2)] is identical to that of the master equation $P_{\mathrm{st}}^{\mathrm{ME}}(x)$. In other words, this FP equation is constructed so as to yield the correct stationary distribution. It follows from Eqs. (13), (14), and (2) that

$$\begin{aligned} A_3(x) &= D(x) \ln \frac{(\alpha + \beta + \gamma)x^2 + \alpha\beta\gamma}{(x^2 + \alpha\beta + \beta\gamma + \gamma\alpha)x} + O(\epsilon) \\ B_3(x) &= 2D(x) + O(\epsilon) \end{aligned} \tag{16}$$

where $D(x)$ is a well-behaved positive function, and is independent of ϵ. For simplicity we assume that $D(x)$ is a constant D. This assumption has only a small affect on the scaling of time and does not affect our essential results on the *system-size dependence* of relaxation times.

For each of the FP equations developed above we can now construct the free-energy-like function $U(x)$ of Eq. (3).[2] Equations (9), (12), and (16) in (3) yield

$$
\begin{aligned}
U_1(x) &= \text{const} - C^{-1}\left(\alpha\beta\gamma x - \frac{\alpha\beta + \beta\gamma + \gamma\alpha}{2}x^2 + \frac{\alpha + \beta + \gamma}{3}x^3 - \frac{x^4}{4}\right) \\
U_2(x) &= \text{const} + 2x - \frac{4\alpha(\beta + \alpha)(\gamma + \alpha)}{(\beta - \alpha)(\gamma - \alpha)}\ln(\alpha + x) \qquad (17) \\
&\quad - \frac{4\beta(\gamma + \beta)(\alpha + \beta)}{(\gamma - \beta)(\alpha - \beta)}\ln(\beta + x) - \frac{4\gamma(\alpha + \gamma)(\beta + \gamma)}{(\alpha - \gamma)(\beta - \gamma)}\ln(\gamma + x) \\
U_3(x) &= \phi_e(x)
\end{aligned}
$$

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[2] In many physical systems the function $U(x)$ is closely related to a free energy, such as, for instance, one of Landau–Ginzburg type. In chemical reaction systems there is no simple free energy function in the thermodynamic sense. However, since the stochastic theory of these systems has the same mathematical structure as the nonequilibrium thermodynamics of other physical systems, we call the function $U(x)$ a free-energy-like function.

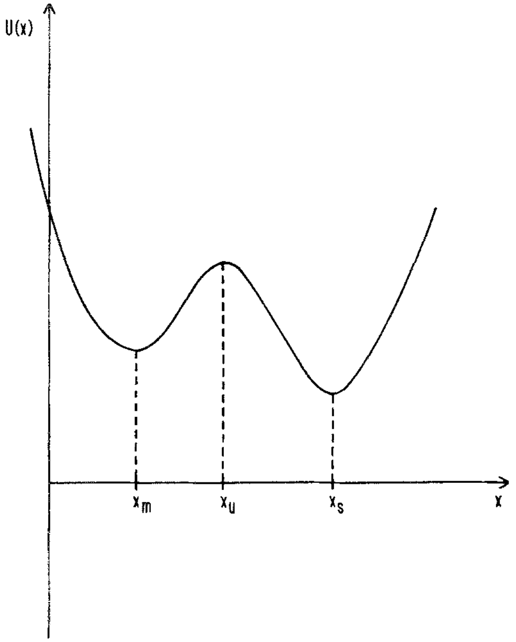

Fig. 2. Free energy function $U(x)$ for the nonlinear system (4). The metastable state is denoted by x_m, the unstable state by x_u, and the stable state by x_s.

The stationary states of the system (4) occur at the extrema of $U(x)$. It is easily shown that the free-energy-like functions $U_1(x)$, $U_2(x)$, and $U_3(x)$ corresponding to FP equations I, II, and III have extrema and thus stationary states at the same locations and of the same nature as those of the master equation (10). These stationary states are shown in Fig. 2. Only the third FP equation, however, has, by construction, the correct stationary distribution with $P_{\text{st}}(x) = P_{\text{st}}^{\text{ME}}(x)$.

3. MEAN FIRST PASSAGE TIMES

In this section we summarize the formulas used to obtain the mean first passage time$^{(14,15)}$ that we will then employ to estimate relaxation times.

The conditional first passage time $T(\xi|x_0)$ is defined as the time when a process crosses $x = \xi$ for the first time given that at time $t = 0$ the process was at $x = x_0$:

$$T(\xi|x_0) \equiv \min\{\tau|X(\tau) = \xi,\ X(0) = x_0\} \tag{18}$$

The probability distribution $\phi(t;\ \xi|x_0)$ for the random variable $T(\xi|x_0)$ is obtained as follows. Let $f(x, t\,|\,x_0)$ be the probability density for the random variable $X(t)$ to have value x without ever having crossed $x = \xi$ in the time interval $(0, t)$, given that $X(0) = x_0$. This probability density is the solution of the FP equation (1), where we now use $f(x, t\,|\,x_0)$ to denote the probability distribution, with initial condition $f(x, 0|x_0) = \delta(x - x_0)$ and with boundary conditions

$$f(\xi, t\,|\,x_0) = 0 \tag{19}$$

$$\left\{\frac{\epsilon}{2}\frac{\partial}{\partial x}[B(x)f(x, t\,|\,x_0)] - A(x)f(x, t\,|\,x_0)\right\}_{x=r} = 0 \tag{20}$$

Equation (19) represents an "absorbing" boundary condition, which simply ensures that the process has not crossed ξ up to time t. Equation (20) is a reflecting boundary condition, with r representing the lower boundary (if $x_0 < \xi$) or the upper boundary (if $x_0 > \xi$) of the domain and where r may be $\pm\infty$. For definiteness we will take $r < x_0 < \xi$.

We next define the cumulative distribution function

$$F(t;\ \xi|x_0) \equiv \int_r^\xi f(x, t\,|\,x_0)\,dx \tag{21}$$

which gives the probability that the random variable $X(\tau)$ never crosses $x = \xi$ during the time interval $0 \leqslant \tau \leqslant t$ given that $X(0) = x_0$. Then it is also true that $F(t;\ \xi|x_0)$ is the probability that the first passage time $T(\xi|x_0)$ is greater than t, i.e.,

$$F(t;\ \xi|x_0) = \operatorname{Prob}\{T(\xi|x_0) > t\,|\,X(0) = x_0\} \tag{22}$$

The probability density for $T(\xi|x_0)$ is then given by

$$\phi(t;\,\xi|x_0) = -\frac{\partial}{\partial t} F(t;\,\xi|x_0) \tag{23}$$

The first passage time moments are obtained from this probability density according to

$$T_n(\xi|x_0) \equiv \int_0^\infty t^n \phi(t;\,\xi|x_0)\,dt \tag{24}$$

To evaluate these moments it is convenient to consider the backward Kolmogorov equation corresponding to the FP equation (1),

$$\frac{\partial f(x,t\,|\,x_0)}{\partial t} = \left[A(x_0)\frac{\partial}{\partial x_0} + \frac{\epsilon}{2} B(x_0)\frac{\partial^2}{\partial {x_0}^2}\right] f(x,t\,|\,x_0) \tag{25}$$

with appropriate boundary conditions in accordance with (19) and (20). Performing the operations indicated in Eqs. (21), (23), and (24) on (25) yields a differential difference equation for the first passage time moments,

$$\frac{\epsilon}{2} B(x_0)\frac{d^2}{d{x_0}^2} T_n(\xi|x_0) + A(x_0)\frac{d}{dx_0} T_n(\xi|x_0) = -nT_{n-1}(\xi|x_0) \tag{26}$$

with boundary conditions

$$T_n(\xi|\xi) = 0, \qquad \frac{d}{dx_0} T_n(\xi|x_0)|_{x_0=r} = 0 \qquad (n \geqslant 1) \tag{27}$$

and with $T_0(\xi|x_0) \equiv 1$.

Of particular interest in this paper is the mean first passage time $T_1(\xi|x_0)$, which we will relate later to characteristic relaxation times. The explicit solution of Eq. (26) for $n = 1$ with boundary conditions (27) is

$$T_1(\xi|x_0) = \frac{2}{\epsilon}\int_{x_0}^{\xi} \exp\left[\frac{1}{\epsilon} U(x)\right] dx \int_r^x \frac{\exp[-(1/\epsilon)U(y)]}{B(y)}\,dy \tag{28}$$

with $U(x)$ and $U(y)$ defined by Eqs. (2) and (3). Equation (28) for the mean first passage time is the main result to be used in our further analysis. It should be noted that the calculation of the mean first passage time, which is an average of the time-dependent function $\phi(t;\,\xi|x_0)$, requires the knowledge of only the equilibrium distribution $P_{\mathrm{st}}(x)$ of the process. Thus, an accurate determination of the free-energy-like function $U(x)$ is all that is required; it is not necessary to solve the full time-dependent FP equation.

4. RELAXATION FROM A METASTABLE STATE

We will now estimate the relaxation time of a system from a metastable state, using the results of the previous sections. A metastable state is shown in Fig. 2 and is defined as a state at which $U(x)$ has a minimum but not an absolute minimum. It is thus a local minimum of the free energy function. Denoting the absolute minimum of $U(x)$ by x_s and the metastable state by x_m, we have

$$\begin{gathered} U'(x_m) = 0, \qquad U''(x_m) > 0 \\ U'(x_s) = 0, \qquad U''(x_s) > 0 \\ U(x_m) > U(x_s) \end{gathered} \tag{29}$$

where the primes denote differentiation with respect to x. For illustrative purposes we will here consider the simplest nonlinear system with a metastable state, namely one that has one metastable, one unstable, and one stable state with $x_m < x_u < x_s$ (see Fig. 2). The system of Section 2 is of this type for appropriate values of α, β, and γ.

To estimate the relaxation time τ_m from the metastable state x_m to the stable state x_s we use the mean first passage time from x_m to the unstable state x_u. This leads to a valid result since the relaxation time from x_u to x_s is negligibly short compared to the time of passage from x_m to x_u.$^{(9)}$ From Eq. (28) we then have

$$\tau_m \equiv T_1(x_u|x_m) = \frac{2}{\epsilon}\int_{x_m}^{x_u} \exp\left[\frac{1}{\epsilon}U(x)\right] dx \int_{-\infty}^{x} \frac{\exp[-(1/\epsilon)U(y)]}{B(y)}\,dy \tag{30}$$

We have taken the lower boundary of the domain of x at $-\infty$.

Our main interest lies in the system-size dependence of τ_m, i.e., in the dependence of τ_m on ϵ. We will establish upper and lower bounds on τ_m such that both bounds have the same dependence on ϵ. This will yield the system-size dependence of τ_m. From the shape of $U(x)$ shown in Fig. 2 it is seen that the relaxation time τ_m is bounded by

$$\tau_m^{(1)} < \tau_m < \tau_m^{(2)} \tag{31}$$

where

$$\tau_m^{(i)} = \frac{2}{\epsilon}\int_{x_m}^{x_u} \exp\left[\frac{1}{\epsilon}U(x)\right] dx \int_{-\infty}^{x^{(i)}} \frac{\exp[-(1/\epsilon)U(y)]}{B(y)}\,dy, \qquad i = 1, 2 \tag{32}$$

and where $x^{(1)} = x_m$ and $x^{(2)} = x_u$. One can place further bounds on the integrals appearing in (32) by noting that the main contribution to the first integral comes from the vicinity of $x = x_u$ and the main contribution to the second integral is from the region around $x = x_m$ since the integrands have sharp maxima at these points. To estimate the first integral in (32) we use the bounds

$$U(x_u) - M_1(x - x_u)^2 \leqslant U(x) \leqslant U(x_u) - m_1(x - x_u)^2 \qquad x_m < x < x_u \tag{33}$$

where M_1 and m_1 are positive constants of $O(\epsilon^0)$. This immediately leads to

$$\mu_1\epsilon^{1/2}\exp\left[\frac{1}{\epsilon}U(x_u)\right] < \int_{x_m}^{x_u}\exp\left[\frac{1}{\epsilon}U(x)\right]dx < \nu_1\epsilon^{1/2}\exp\left[\frac{1}{\epsilon}U(x_u)\right] \qquad (34)$$

where μ_1 and ν_1 are positive constants of $O(\epsilon^0)$ related to M_1 and m_1. To estimate the second integral in (32) the appropriate bounds are

$$U(x_m) + m_2(x - x_m)^2 \leqslant U(x) \leqslant U(x_m) + M_2(x - x_m)^2$$
$$x_m - c < x < x_u \qquad (35)$$

where c, m_2, and M_2 are positive constants of $O(\epsilon^0)$. These bounds in turn restrict the second integral in (32),

$$\mu_2^{(i)}\epsilon^{1/2}\exp\left[-\frac{1}{\epsilon}U(x_m)\right] < \int_{-\infty}^{x^{(i)}}\frac{\exp[-(1/\epsilon)U(x)]}{B(x)}\,dx$$
$$< \nu_2^{(i)}\epsilon^{1/2}\exp\left[-\frac{1}{\epsilon}U(x_m)\right] \qquad (36)$$

where $\mu_2^{(i)}$ and $\nu_2^{(i)}$ are positive constants of $O(\epsilon^0)$. We have assumed that the ϵ-independent function $B(x)$ is a slowly varying function of x compared to the variation of the numerator of the integrand near x_m [cf. Eqs. (9), (12), and (16)].

It is now a straightforward matter to establish that (34) and (36) in (32) yield bounds $\tau_m^{(1)}$ and $\tau_m^{(2)}$ for the relaxation time τ_m that are of the same order of magnitude in ϵ. It therefore follows that τ_m must have the same behavior, given by

$$\tau_m = K\exp\{(1/\epsilon)[U(x_u) - U(x_m)]\} \qquad (37)$$

where the coefficient K is of $O(\epsilon^0)$.

The relaxation time from a metastable state thus grows exponentially with system size, a conclusion that has also been reached for other models and by other methods.(3,6,8-10) The form of Eq. (37) shows the sensitive dependence of the relaxation time on the barrier height $[U(x_u) - U(x_m)]$, a result which has also been pointed out previously.(13) This dimensionless barrier height is thus *the* important feature of the system that one must determine accurately in order to obtain the correct relaxation time from a metastable state. It is therefore necessary to choose a FP equation whose free energy function not only correctly locates the stable, metastable, and unstable extrema in agreement with the deterministic rate equation or the corresponding master equation, *but whose free energy function has the correct magnitude at these extrema.*

In view of these requirements, only the third of the three FP equations discussed in Section 2 yields the correct relaxation time from a metastable state, since it has been specifically constructed to yield the correct values of the free energy function $U(x)$ at the extrema. It is a simple matter to check that the first and second FP equations of Section 2 do not yield the correct dimensionless barrier height $[U(x_u) - U(x_m)]$. Since the relaxation time from an unstable state, i.e., a maximum of the potential, does not depend upon the barrier height, one would expect that all three FP equations will yield the identical system-size dependence of the relaxation time from an unstable state.

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