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Relative Stability of Multiple Stationary States Related to Fluctuations

Nancy Fisher Hansen and John Ross*

Department of Chemistry, Stanford University Stanford, California 94305-5080

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We apply the eikonal approximation to the stochastic master equation for reaction−diffusion systems. Its stationary solution is expressed as an excess work and is shown to be a Lyapunov function for the deterministic evolution of inhomogeneous systems. From this result we establish a new stochastic criterion of relative stability and equistability of systems with multiple homogeneous stationary states in terms of inhomogeneous fluctuations.

I. Introduction

Chemical systems with nonlinear kinetics may have multiple stationary states for given constraints that maintain the system far from equilibrium. The relative stability of such multiple stationary states has been discussed in prior studies.[1−3] Consider an experimental arrangement in which a system with two stable stationary states and one unstable stationary state is maintained in one of its stable stationary states (SS1) in one-half of a large container (see Figure 1) and the other half contains the system in its other stable stationary state (SS3). On removal of a partition separating these two stationary states, a smooth concentration profile will develop since the concentration of any intermediate species in stable stationary state 1 is likely to be different from that in stable stationary state 3. Then one of three possibilities will occur: the profile will travel in the direction of increasing the domain of the more stable stationary state (either SS1 or SS3). However, at equistability of the two stationary states, the velocity of the developed front is zero. This result can be obtained from the solution of deterministic reaction−diffusion equations and has been tested in experiments.[4,5]

The deterministic reaction−diffusion equations have an infinity of Lyapunov functions that are evolution criteria for the deterministic motion, such as front propagation in either direction in the system just discussed. In ref 1 we showed that any Lyapunov function Φ that can be expressed as an integral along the deterministic path of the system correctly predicts the observed relative stability of two steady states in the limit of large systems. One such Lyapunov function is an excess work Φ_{det}, which has been defined by means of the deterministic reaction−diffusion equations.[6−11] Φ_{det} is not a state function but is fully defined along the deterministic trajectories. It is, in general, not related to fluctuations in nonlinear systems, i.e., to stationary solutions of the stochastic master equations.

Stationary solutions of the master equations for multivariable homogeneous chemical systems far from equilibrium can be discussed, in the eikonal approximation, in terms of an excess work Φ^0, which is a state function, a Lyapunov function for the stable stationary states of the system, and is, to logarithmic accuracy, a solution of the master equation, as shown for homogeneous systems of this kind.[12−14]

In the present work, we apply the eikonal approximation to the stochastic master equation for reaction−diffusion systems and, thus, extend the concept of the excess work Φ^0 to such systems. We show that Φ^0 is a stationary solution of the master equation, a Lyapunov function for the deterministic evolution of inhomogeneous reaction−diffusion systems, and a criterion of relative stability for multiple stationary states in such systems. Thus, we obtain an important new view of relative stability and equistability of systems with multiple homogeneous stationary states in terms of inhomogeneous fluctuations in these systems.

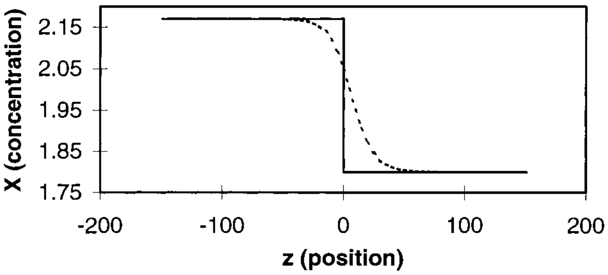

Figure 1. Initially (—) the left half of the system has the concentration values of stationary state 1 and the right half of the system has the concentration values of stationary state 3. At equistability, evolution of the system according to the deterministic equations of motions leads to the stable front (···) shown.

II. The System

We will briefly describe the reaction−diffusion system. Consider as a sufficient example for any multivariable system the isothermal Sel'kov model with rate coefficients and constant concentrations of A and B chosen such that there are three stationary-state solutions of the homogeneous reaction equations (i.e., the rate equations with no diffusion terms). Two of these states, (X^1,Y^1) and (X^3,Y^3), are stable and the other, (X^2,Y^2), is unstable.

The equations given in eq 1 are for a system residing in one spatial dimension. The extension to a three-dimensional system

$$\mathrm{A} \underset{k_2}{\overset{k_1}{\rightleftharpoons}} \mathrm{X} \qquad 2\mathrm{Y} + \mathrm{X} \underset{k_4}{\overset{k_3}{\rightleftharpoons}} 3\mathrm{Y} \qquad \mathrm{Y} \underset{k_6}{\overset{k_5}{\rightleftharpoons}} \mathrm{B} \tag{1}$$

is straightforward. The partial differential equations that represent the reaction−diffusion equations for this model can be transformed into ordinary differential equations by discretizing the spatial variable z into increments small enough that X

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* To whom correspondence should be addressed.

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TABLE 1: Elementary Reactions for a Sel'kov Model System Distributed in One Dimension[a]

elementary reaction	r_x and r_y	$W(x,y;\, r_x,\, r_y)$
$A \rightarrow X_i$	$r_{x,i} = +1$	$k_1 A$
$X_i \rightarrow A$	$r_{x,i} = -1$	$k_2 X_i$
$X_i + 2Y_i \rightarrow 3Y_i$	$r_{x,i} = -1$ $r_{y,i} = +1$	$k_3 X_i Y_i^2$
$3Y_i \rightarrow X_i + 2Y_i$	$r_{x,i} = +1$ $r_{y,i} = -1$	$k_4 Y_i^3$
$Y_i \rightarrow B$	$r_{y,i} = -1$	$k_5 Y_i$
$B \rightarrow Y_i$	$r_{y,i} = +1$	$k_6 B$
$X_0 \rightarrow X_1$	$r_{x,1} = +1$	$d_X X_0$
$X_1 \rightarrow X_0$	$r_{x,1} = -1$	$d_X X_1$
$Y_0 \rightarrow Y_1$	$r_{y,1} = +1$	$d_Y Y_0$
$Y_1 \rightarrow Y_0$	$r_{y,1} = -1$	$d_Y Y_1$
$X_i \rightarrow X_{i+1}$	$r_{x,i} = -1$ $r_{x,i+1} = +1$	$d_X X_i$
$X_{i+1} \rightarrow X_i$	$r_{x,i} = +1$ $r_{x,i+1} = -1$	$d_X X_{i+1}$
$Y_i \rightarrow Y_{i+1}$	$r_{y,i} = -1$ $r_{y,i+1} = +1$	$d_Y Y_i$
$Y_{i+1} \rightarrow Y_i$	$r_{y,i} = +1$ $r_{y,i+1} = -1$	$d_Y Y_{i+1}$

[a] All reactions including species with an index *i* denote *N* reactions, one for each box. The terms *W* are the transition probabilities in the master equation, eq 4.

and Y are essentially constant in a given increment. Labeling the various increments with the index *i* and the increment Δz, we have

$$L = N\Delta z \qquad z_i = i\Delta z \qquad z_0 = 0,\, z_N = L \tag{2}$$

and the deterministic reaction−diffusion equations become

$$\frac{dX_i}{dt} = k_1 A - k_2 X_i - k_3 X_i Y_i^2 + k_4 Y_i^3 + \frac{D_X}{\Delta z^2}(X_{i+1} - 2X_i + X_{i-1})$$

$$\frac{dY_i}{dt} = k_6 B - k_5 Y_i - k_3 X_i Y_i^2 - k_4 Y_i^3 + \frac{D_Y}{\Delta z^2}(Y_{i+1} - 2Y_i + Y_{i-1}) \tag{3}$$

To examine the relative stability of the stable steady states, we take the requirement that the concentrations of X and Y at the left side of the system are held fixed at the values of one stable steady state and at the right they have the values of the other steady state, i.e., $(X_0,Y_0) = (X^1,Y^1)$ and $(X_{N+1},Y_{N+1}) = (X^3,Y^3)$ for all *t*, as boundary conditions for the system. As an initial condition, one-half of the system is given the value of stable steady-state 1 (SS1) and the other half is given the value of stable steady-state 3 (SS3) (see Figure 1). When the system is allowed to evolve according to eq 3, a continuous front forms at the point of discontinuity and, depending on the relative stability of the stable steady states, travels without changing form in the direction that creates the more stable state. If the parameters dictate that the continuous front does not travel, the system is said to be "at equistability."

III. Eikonal Approximation to the Stochastic Master Equation for Reaction−Diffusion Systems

The behavior of the two species in each of the *N* boxes described in the last section is given by the $10N + 4$ elementary reactions in Table 1 and as a whole the system obeys the master equation

$$\frac{\partial P(\vec{X},\vec{Y};t)}{\partial t} = \sum_{r_x,r_y}[W(\vec{X} - \vec{r}_X,\, \vec{Y} - \vec{r}_Y; \vec{r}_X, \vec{r}_Y)P(\vec{X},\vec{Y};t) - W(\vec{X},\vec{Y};\vec{r}_X,\vec{r}_Y)P(\vec{X},\vec{Y};t)] \tag{4}$$

where the sum is over the elementary reactions listed in Table 1, and we denote the set of concentration values $(X_i,\, Y_i)$ in the *N* boxes as vectors $\vec{W}$ and $\vec{Y}$. $W(\vec{X},\vec{Y};\vec{r}_x,\vec{r}_y)$ is the probability per unit time of a transition from $(\vec{X},\vec{Y})$ to $(\vec{X} + \vec{r}_x, \vec{Y} + \vec{r}_y)$.

According to the eikonal (instanton) approximation, the stationary distribution about the *n*th attractor (stable state of the entire system) is given by

$$P^{(n)}(\vec{X},\vec{Y}) = C^{(n)} \exp(-S_n(\vec{X},\vec{Y})) \tag{5}$$

$$S_n(\vec{X}^{(n)}_{st}, \vec{Y}^{(n)}_{st}) = 0$$

$$H(\vec{x},\, \vec{y};\, \nabla_{\vec{x}} s_n(\vec{x},\, \vec{y}),\, \nabla_{\vec{y}} s_n(\vec{x},\, \vec{y})) = 0$$

$$H(\vec{x},\, \vec{y};\, \vec{p}_x,\, \vec{p}_y) = \sum_{r_x,r_y} w(\vec{x},\, \vec{y};\, \vec{r}_x,\, \vec{r}_y)(\exp(\vec{r}_x\cdot\vec{p}_x + \vec{r}_y\cdot\vec{p}_y) - 1) \tag{6}$$

$$\vec{p}_x \equiv \nabla_{\vec{x}} s_n(\vec{x},\, \vec{y}),\, \vec{p}_y \equiv \nabla_{\vec{y}} s_n(\vec{x},\, \vec{y})$$

where s_n is obtained by solving Hamilton's equations of motion for the Hamiltonian *H*.

Here we have defined the symbols

$$\vec{x} \equiv \vec{X}/\Omega,\, \vec{y} \equiv \vec{Y}/\Omega,\, w(\vec{x},\, \vec{y};\, \vec{r}_x,\, \vec{r}_y) \equiv W(\vec{X},\, \vec{Y};\, \vec{r}_x,\, \vec{r}_y)\Omega \tag{7}$$

and

$$s_n(\vec{x},\, \vec{y}) \equiv S_n(\vec{X},\vec{Y})/\Omega \tag{8}$$

and the dot product has the usual vector meaning given by

$$\vec{f}\cdot\vec{g} \equiv \sum_{i=1}^{N} f_i g_i \tag{9}$$

The sum is over values for all *N* boxes. Ω is the volume of the system. These equations of motion have the form

$$\dot{x}_i = \sum_{r_x,r_y} r_{x,i} w(\vec{x},\, \vec{y};\, \vec{r}_x,\, \vec{r}_y) \exp(\vec{r}_x\cdot\vec{p}_x + \vec{r}_y\cdot\vec{p}_y)$$

$$\dot{y}_i = \sum_{r_x,r_y} r_{x,i} w(\vec{x},\, \vec{y};\, \vec{r}_x,\, \vec{r}_y) \exp(\vec{r}_x\cdot\vec{p}_x + \vec{r}_y\cdot\vec{p}_y) \tag{10}$$

$$\dot{p}_{x,i} = -\sum_{r_x,r_y} (\exp(\vec{r}_x\cdot\vec{p}_x + \vec{r}_y\cdot\vec{p}_y) - 1)\nabla_{x,i} w(\vec{x},\, \vec{y};\, \vec{r}_x,\, \vec{r}_y)$$

$$\dot{p}_{y,i} = -\sum_{r_x,r_y} (\exp(\vec{r}_x\cdot\vec{p}_x + \vec{r}_y\cdot\vec{p}_y) - 1)\nabla_{x,i} w(\vec{x},\, \vec{y};\, \vec{r}_x,\, \vec{r}_y)$$

where the sum over r_x and r_y is a sum over all elementary reactions listed in Table 1. The action s_n can be obtained from the expression

$$s_n(\vec{x}(t),\vec{y}(t)) = \int_{t_0}^{t} \mathrm{d}t'(\vec{p}_x\cdot\dot{\vec{x}} + \vec{p}_y\cdot\dot{\vec{y}}) \tag{11}$$

$$= \int_{t_0}^{t} \mathrm{d}t' \sum_{r_x,r_y} (\vec{r}_x\cdot\vec{p}_x + \vec{r}_y\cdot\vec{p}_y) w(\vec{x}, \vec{y}; \vec{r}_x, \vec{r}_y) \times \exp(\vec{r}_x\cdot\vec{p}_x + \vec{r}_y\cdot\vec{p}_y)$$

$$= \int_{t_0}^{t} \mathrm{d}t' \sum_{r_x,r_y} [(\vec{r}_x\cdot\vec{p}_x + \vec{r}_y\cdot\vec{p}_y) \exp(\vec{r}_x\cdot\vec{p}_x + \vec{r}_y\cdot\vec{p}_y) + 1 - \exp(\vec{r}_x\cdot\vec{p}_x + \vec{r}_y\cdot\vec{p}_y)] w(\vec{x}, \vec{y}; \vec{r}_x, \vec{r}_y)$$

We have made use of the relation $H(x,p) = 0$, subtracting H in the third line. Using the inequality $x \exp(x) + 1 - \exp(x) \geq 0$ and the fact that w is always positive, this equation makes it clear that along a fluctuational path away from the stationary state and determined by Hamilton's equations of motion, we have

$$\left.\frac{\mathrm{d}s_n(\vec{x}(t),\vec{y}(t))}{\mathrm{d}t}\right|_{\mathrm{fluc}} \geq 0 \tag{12}$$

A still more important fact for our later analysis is that

$$\left.\frac{\mathrm{d}s_n(\vec{x},\vec{y})}{\mathrm{d}t}\right|_{\mathrm{det}} = \nabla_{\vec{x}} s_n(\vec{x},\vec{y})\cdot\left.\frac{\mathrm{d}\vec{x}}{\mathrm{d}t}\right|_{\mathrm{det}} + \nabla_{\vec{y}} s_n(\vec{x},\vec{y})\cdot\left.\frac{\mathrm{d}\vec{y}(\vec{x},\vec{y})}{\mathrm{d}t}\right|_{\mathrm{det}}$$

$$= \sum_{r_x,r_y} \vec{p}_x\cdot\vec{r}_x w(\vec{x}, \vec{y}; \vec{r}_x, \vec{r}_y) + \vec{p}_y\cdot\vec{r}_y w(\vec{x}, \vec{y}; \vec{r}_x, \vec{r}_y) \tag{13}$$

$$= \sum_{r_x,r_y} (\vec{p}_x\cdot\vec{r}_x + \vec{p}_y\cdot\vec{r}_y + 1 - \exp(\vec{p}_x\cdot\vec{r}_x + \vec{p}_y\cdot\vec{r}_y)) w(\vec{x}, \vec{y}; \vec{r}_x, \vec{r}_y)$$

We have made use of the relations $p = \nabla s_n(x)$ and $H(x,p) = 0$. Now using the inequality, $x + 1 - \exp(x) \leq 0$, we see that

$$\left.\frac{\mathrm{d}s_n(\vec{x},\vec{y})}{\mathrm{d}t}\right|_{\mathrm{det}} \leq 0 \tag{14}$$

Hence, the stationary solution to the master equation, $s_n(x,y)$, is a Lyapunov function for the deterministic path from (x,y) to the attractor of the stable stationary state.

IV. Thermodynamic Analysis of a Reaction−Diffusion System

In ref 12, a connection was made between the stationary solution $s_n(x,y)$ for a homogeneous system and a thermodynamic excess work function ϕ^0. For a system with two intermediates x and y, for example, we can write

$$\mathrm{d}s = \frac{1}{kTV}\,\mathrm{d}\phi^0$$

$$= (\mu_x - \mu_{x0})\,\mathrm{d}n_{x,fl} + (\mu_y - \mu_{y0})\,\mathrm{d}n_{y,fl} \tag{15}$$

where (x^0,y^0) define a reference state according to the equations

$$p_x = \ln(x/x^0) \tag{16}$$

$$p_y = \ln(y/y^0)$$

which hold for an equivalent linear system.

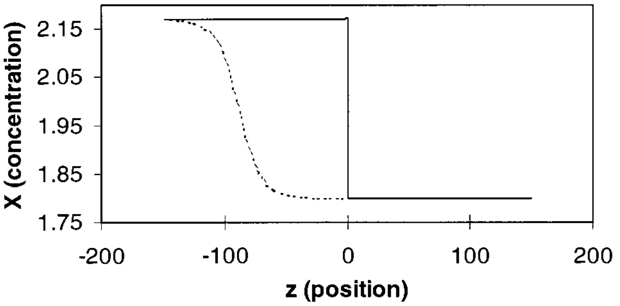

Figure 2. Translation of the front to the left side of the system has a change in Φ^0 of $\Delta\Phi^0 = 0$. The same is true for translation to the right side.

The displacements $\mathrm{d}n_x$, $\mathrm{d}n_y$, etc., are along the most probable fluctuational path. Since the momentum p is the gradient of the action, $\mathrm{d}s$ and therefore $\mathrm{d}\phi^0$, are exact differentials.

For a system of N boxes distributed in one dimension, the state function of the total excess work is the sum of that in each box, eq 17. The reference state (X^0,Y^0) is determined

$$\Phi^0(X,Y) = \int_s^{(X,Y)} \sum_{i=1}^{N} kTV\,\mathrm{d}\phi_i^0 \tag{17}$$

$$= kTV \sum_{i=1}^{N} [\int_s^{(X,Y)} \mathrm{d}X_i \ln(X_i/X_i^0) + \mathrm{d}Y_i \ln(Y_i/Y_i^0)]$$

according to the same prescription as in the homogeneous case, except now in the full $2N$-dimensional space. Since $\mathrm{d}\phi$ is an exact differential, we can choose to perform the integration along the deterministic path.

V. Condition for Equistability in Terms of Fluctuations

Figure 1 shows the resulting stable front when a system at equistability is allowed to evolve deterministically from a discontinuous initial state with SS1 in the left half of the system and SS3 in the right half. This process results in a change in the thermodynamic excess work function Φ^0. But at equistability, translation of the entire front to the left or the right does not change the value of Φ^0. This can be understood by considering the cases in which the control parameter is infinitesimally smaller or larger than its value at equistability. If SS1 is slightly more stable than SS3, the deterministic motion of the front will be a translation to the right. Since Φ^0 is a Lyapunov function for the system, $\Delta\Phi^0$ for this process must be negative. Likewise, if SS3 is more stable than SS1, a translation of the front to the left will also result in a negative $\Delta\Phi^0$. So at equistability, the limiting value of $\Delta\Phi^0$ for an exact translation must be zero.

Since Φ^0 is a state function, its value for a change from all SS1 to a stable front in the left half of the system only (see Figure 2) is equal to the sum of $\Delta\Phi^0$ for the creation of the front from the discontinuity and zero for the translation of the front. This is exactly the value for a change from SS3 to a stable front in the right half of the system. Therefore

$$\Delta\Phi^0(SS1 \rightarrow SF) = \Delta\Phi^0(SS3 \rightarrow SF) \tag{18}$$

and, since Φ^0 is a state function, we have

$$\Delta\Phi^0(SF \rightarrow SS1) = \Delta\Phi^0(SF \rightarrow SS3) \tag{19}$$

We see that the stationary probability distribution of the master equation in the eikonal approximation Φ^0 is not only a Lyapunov function for the deterministic reaction−diffusion equations, but also provides a measure of the relative stability and equistability as interpreted by inhomogeneous fluctuations. There is, thus, an analogy of equistability in systems with multiple steady states and phase bistability at equilibrium. As an example, an experiment conducted with liquid water and water vapor as outlined in the discussion of Figure 1 shows propagation of the phase front in either one or the other direction but at equilibrium the front velocity is zero. Further, at equilibrium the probability of a fluctuation converting one phase to the other equals that of the reverse process.

In this work, we provide an additional physical meaning of equistability. At equistability, the probability of a fluctuation from the stable front to all steady-state 1 is equal to the probability of a fluctuation from the stable front to all steady-state 3, eq 19. Thus, we have established a new criterion of equistability of multiple stationary states, one in terms of inhomogeneous fluctuations in such systems.

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