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A Thermodynamic Variational Principle in Nonlinear Systems Far from Equilibrium

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The simplest viewpoint of nonlinear systems far from equilibrium suggests that the state of maximum entropy production is most stable among various possible metastable states under external perturbation for immobile boundaries, and that the shape with maximum increasing rate of entropy production is stabilized for mobile boundaries. Examples of computer simulation are demonstrated for a chemical structure and a growing random pattern.

KEY WORDS: Relative stability; metastable states; maximum entropy production; growing random pattern; surface kinetic dimension.

1. INTRODUCTION

The formation of macroscopic patterns is a fascinating phenomenon characteristic of nonlinear systems far from equilibrium. Examples including well-known Benard convection are common to our daily life. Individual mechanisms which lead to their structures have mostly been understood so far as the onset is concerned. When the system is subject to a boundary condition farther and farther from thermal equilibrium, the system generally evolves to a more and more complicated structure. The structure in general depends on the initial and boundary conditions, and cannot be obtained analytically.

As for Benard convection the pattern formation has been fairly well studied both theoretically and experimentally. The pattern formed by the velocity field of convecting fluid in a system of a large aspect ratio is quite complex, as observed experimentally by J. P. Gollub, A. R. McCarriar, and

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J. F. Steinman[1] and by V. Croquette, M. Mory, and F. Schosseler.[2] H. S. Greenside, W. M. Coughran, and N. L. Schryer[3] have succeeded in reproducing most of the features observed experimentally by computer simulation based on the amplitude equation. Y. Pomeau and P. Manneville[4] have discussed the selection of the unique wavelength among various ones possible in linear theory. In a simple case a Lyapounov functional exists and the steady state corresponds to the minimum of the functional. The contribution from the boundaries, bending and defects in the texture was discussed by M. C. Cross.[5] In the more general case when there is no Lyapounov functional one has to depend on numerical calculation to obtain the preferred structure.

In dendritic crystal growth J. S. Langer and H. Muller-Krumbhaar[6] have proposed the "marginal stability hypothesis" for the mode selection. The nonlinear mechanism to stabilize this selected mode is not known at the present stage.[7] Thus, it is not possible at present to obtain analytically the preferred mode of the pattern except for some special cases. Also there is no common physical understanding for the stability of the selected patterns in general for the nonlinear systems far from equilibrium.

In this paper I would like to review a simple thermodynamic viewpoint which the author has proposed and to present some examples of numerical calculations for the stability of steady states and growing patterns.

2. A THERMODYNAMIC VIEWPOINT

One of the simplest viewpoints for a nonequilibrium system is to look at a total system consisting of the nonlinear system (hereafter n-system) under consideration and several thermodynamic reservoirs in contact with the n-system as a closed system. There, the reservoirs, each of which has different thermodynamic quantity, are very large but finite. We discuss a simple case where the evolution of the total system is described by its phase space volume. Then, for a proper time scale the entropy of the total system is a monotonic function of time. One might argue more strongly that the system has the highest probability of choosing the path for which the entropy increment of the total system is maximized if some conditions for the time scales are satisfied.[8] This choice of the path shares a common basis with the second law of thermodynamics, but it was naturally not stressed in equilibrium thermodynamics. For nonequilibrium phenomena this choice of the path plays an important role. For a system in contact with more than two immobile boundaries such as the Benard convection system there is a time domain for which the n-system behaves asymptotically steadily, if the reservoirs are large enough. One may argue that the most stable state corresponds to the state of the maximum entropy production for the n-system, since all the reservoirs are assumed to be ideal. This variational principle is equivalent to the "energy flow maximum principle" which A. J. Lotka proposed for the evolution of biological systems[9] and to the "principe de facilitation" which M. N. J. Felici has proposed.[10]

For a system which has growing boundaries such as crystal growth, there is a time domain in which the entropy production varies as a power of time. We argue here that the mode of growth is most stabilized when the exponent of the increment of the entropy production is maximized.

In the next section we demonstrate some examples of numerical calculation which are in agreement with this simple viewpoint.

3. RELATIVE STABILITY AMONG VARIOUS POSSIBLE STEADY STATES

Recently M. Suzuki and the author[11] have investigated relative stability among various metastable states of a convecting charged fluid system by computer simulation. They have found that the most probable state in the presence of external noise lies in the region corresponding to the maximum current carrying states within the computational error. H. S. Greenside, W. M. Coughran, and N. L. Schryer[3] have found in their computer simulation for the evolution of the convecting pattern that the heat current increases monotonically with time and that the steady states would correspond to the maximum heat transport.

Here we would like to discuss relative stability among various metastable states of a chemical reaction system. Let us consider 51 cells of a Brusselator chemical reaction system coupled one dimensionally. By adjusting initial conditions for the distribution of an intermediate x one can

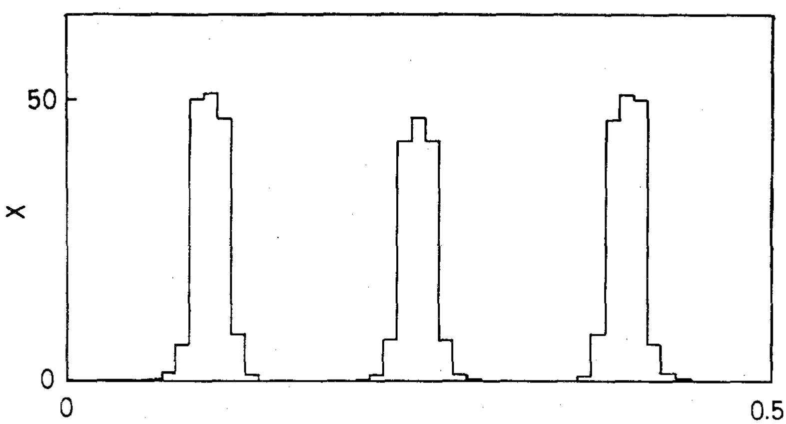

Fig. 1. An example of the structure in the concentration of an intermediate X of linearly coupled Brusselator reaction cells. $N_p = 3$, $\lambda_p = 0.15$.

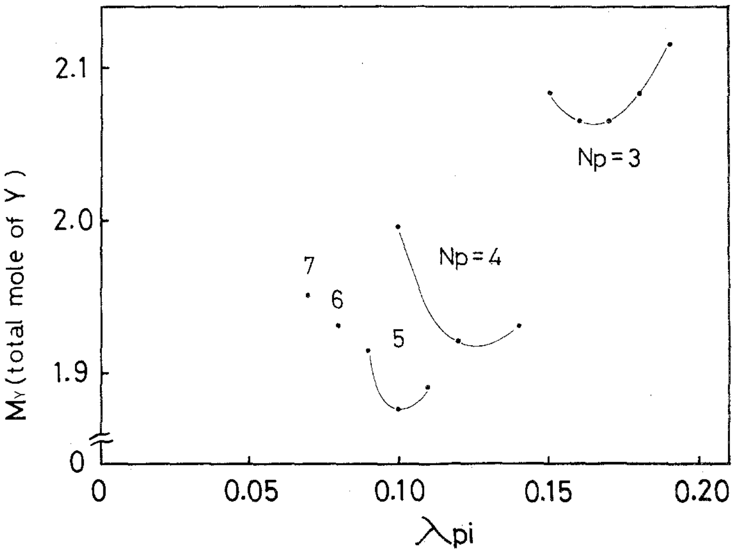

Fig. 2. Total mole of the intermediate Y for the various steady states. The minimum of M_y corresponds to the maximum of the entropy production for the Brusselator.

obtain several metastable states such as shown in Fig. 1.[12] The numbers of possible metastable states, each of which is specified by the peak number N_p and the spacing between the peak λ_p, are found to be $5,3,3,1,1$ for $N_p = 3,4,5,6,7$, respectively. For other N_p one cannot find any metastable state. We have examined relative stability among these metastable states by applying external perturbation. For this purpose one of the source concentrations B was fluctuated, to cause a transition from one (N_p, λ_p) state to the other state. After many runs the probability for each state to appear was measured, and it was found to peak at $N_p = 5$, and $\lambda_p = 0.10$. Simultaneously the entropy production for each steady state was computed. To obtain high accuracy in computation, we calculated the total mole number of the intermediate Y instead of calculating the entropy production directly, since a simple relation is known between them for the Brusselator.[13] As is shown in Fig. 2 the mole M_y was found to take a minimum value, which, in turn, means the maximum value for the entropy production.[12] This is an example of a chemical reaction structure whose stability may be discussed in terms of the variational principle.

4. STABILITY OF A GROWING RANDOM PATTERN

In this section we would like to discuss the relation of the stability of a growing pattern to the variational viewpoint. Figure 3 shows an example of

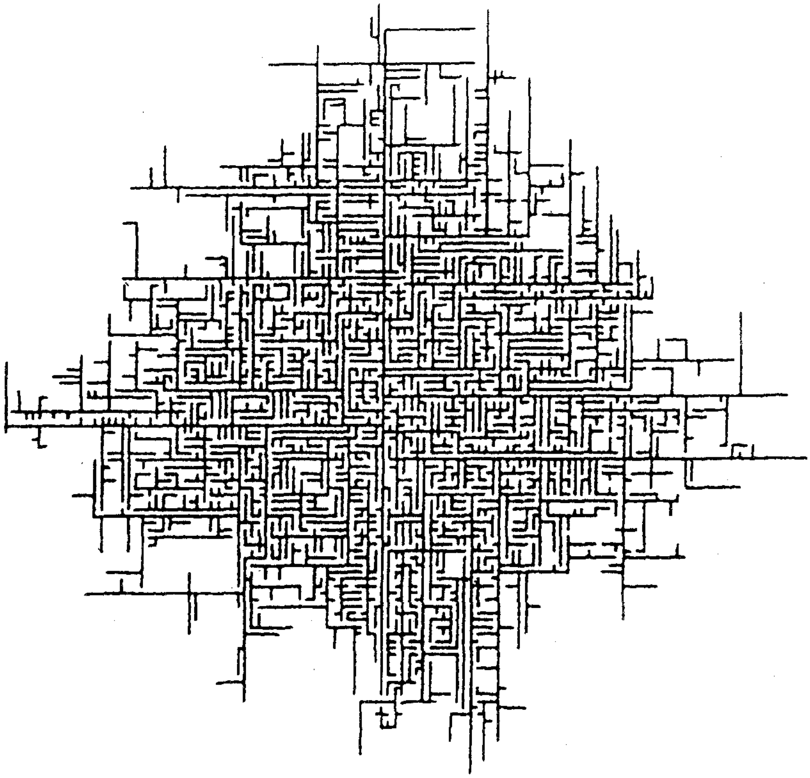

Fig. 3. An example of a growing pattern based on the "hot tip model" $R = 40$, $V = 5000$.

a randomly growing pattern based on the "hot tip model".[14] In this model the pattern grows from a seed crystal at the center by randomly crystallizing its periphery. The parameter corresponding to the Rayleigh number in the convection is the "tip priority factor" R by which the tips grow faster compared to the other sites. The fractal properties of this growing pattern have been studied in detail.[14] Here we focus our attention on the nonequilibrium property of the pattern. We define the "surface kinetic dimension" $D_{sk} = d(\partial \log S / \partial \log V)$, which measures the logarithmic increment of the surface S with respect to that of the volume V. This dimension is 1 for a two-dimensional compact growth and 2 for an extremely ramified structure. It can be shown that the larger the increasing rate of crystallization with respect to time the larger the surface kinetic dimension. Figure 4 shows the D_{sk}^{-1} measured from the patterns as a function of the tip priority factor R. Two breaks are observed in the figure. The first break occurs at $R = 5$. This break was found to correspond to a kinetic surface roughening transition. The second break occurs at about $R = 35$. This was associated with the

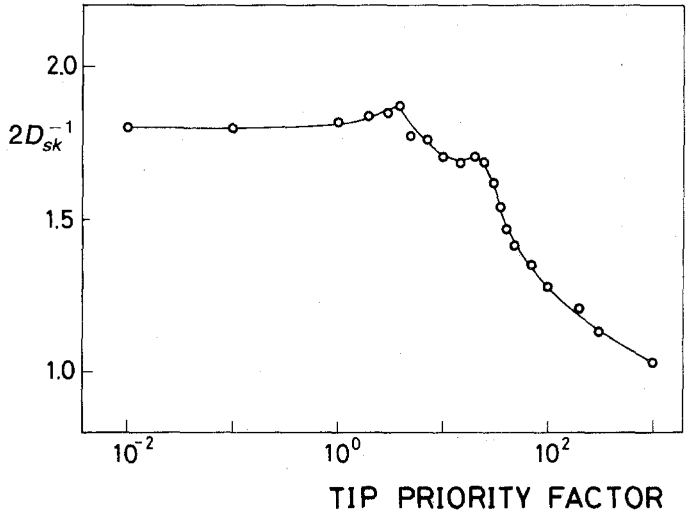

Fig. 4. The inverse of surface kinetic dimension D_{sk} measured from the pattern produced by computer simulation for various values of R.

"bulk to dendritic" transition. These transitions are important in relation to crystal growth and are described elsewhere in detail.[15] Here we wish to focus only on the observation that the transitions tend to increase the surface kinetic dimension D_{sk}, or to increase the increasing rate of crystallization, therefore of the entropy production.

In the examples cited above we have seen that a variational viewpoint is effective for simple cases. In fact phenomena obeying this variational principle seem to dominate the lively part of nature, although counter-examples are not negligible as for the case in the presence of hysteresis. We believe it would be more efficient for the physical understanding of nonequilibrium phenomena to discuss the reason for the deviation from this variational principle, if any, than to discuss each problem separately.

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