A FAREY TRIANGLE IN THE BELOUSOV–ZHABOTINSKII REACTION

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Received 7 July 1986; revised manuscript received 14 October 1986; accepted for publication 21 October 1986

In a recent study Kim and Ostlund, motivated by an interest in frequency locking on a three-torus, constructed a Farey triangle to obtain rational approximants of pairs of irrational numbers that are mutually irrational. We find that their Farey triangle provides a natural compact description of sequences of periodic states observed in our experiments on the Belousov–Zhabotinskii reaction.

Multipeaked periodic waveforms consisting of combinations of large and small amplitude oscillations have been observed in many experiments on nonequilibrium chemical reactions. In fact, sequences of multipeaked periodic states have been observed much more frequently than chaos in nonequilibrium chemical reactions, but extensive theoretical and experimental studies of chaos in recent years have led to a better understanding of the chaotic behavior than the periodic sequences.

Fig. 1 shows some examples of multipeaked periodic waveforms observed in our experiments on the manganese-catalyzed Belousov–Zhabotinskii reaction in a stirred flow reactor. The time series in fig. 1a is formed from the repetition of *two* basic patterns, 3^1 and 2^1, where 3^1 means 3 large oscillations followed by 1 small amplitude oscillation, etc. The time series in fig. 1b consists of repetitions of *three* basic patterns, and in fig. 1c, *four* basic patterns.

In an earlier study [1], we found that an observed sequence of periodic states consisting of two basic patterns could be described by the Farey arithmetic that provides rational approximations of irrational numbers [2]. In the Farey analysis an infinite tree of rational numbers can be constructed from a pair of rational numbers: the Farey sum of the pair p/q and p'/q' is $(p+p')/(q+q')$, which is the rational mediant between p/q and p'/q' with the smallest denominator. This Farey addition can be continued indefinitely, yielding the Farey tree. In our study we found that ion some cases the data went down several levels in the Farey tree.

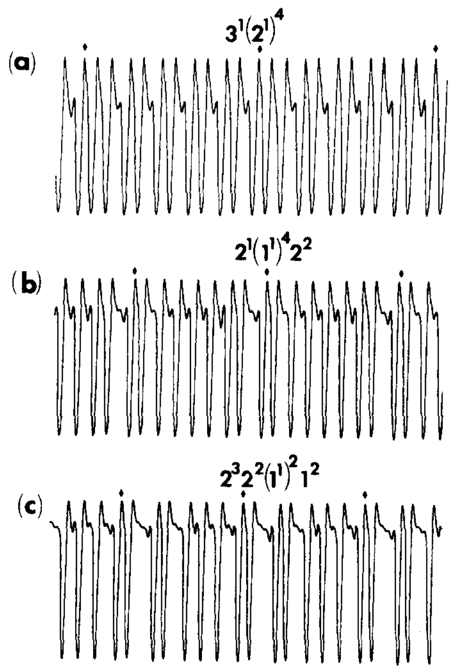

Fig. 1. Bromide ion potential time series showing multipeaked periodic waveforms consisting of combinations of a few basic patterns: (a) two basic patterns, 3^1 and 2^1; (b) three basic patterns, 2^1, 1^1, and 2^2; (c) four basic patterns, 2^3, 2^2, 1^1, and 1^2. The malonic acid concentration and the residence time (reactor volume divided by the total flow rate) in each case was, respectively, (a) 0.033 M, 590 s; (b) 0.046 M, 494 s; (c) 0.053 M, 450 s. For all three cases the concentrations of the other feed chemicals in the reactor were 0.00416 M $MnSO_4$, 1.5 M H_2SO_4 and 0.033 M $KBrO_3$.

Recently Kim and Ostlund [3], motivated by the current interest in frequency locking in multifrequency dynamical systems, have examined rational approximants for two or more mutually irrational numbers. In this analysis rational approximants for pairs of irrational numbers p/q and q/r where p, q and r are relatively prime integers) are represented by triplets (p, q, r) that are organized on a two-dimensional Farey tree, a Farey *triangle.*

We find that the Farey arithmetic discussed by Kim and Ostlund provides a compact description of the observed sequences of periodic states with waveforms consisting of combinations of three basic patterns. In our study of a sequence of periodic states consisting of two basic patterns [1,4], it was sufficient to vary a single control parameter to understand the relation of the sequence to the Farey arithmetic for approximating individual rational numbers. However, in order to relate the sequences of states with waveforms consisting of three basic patterns to Farey triangles, it has been necessary to make measurements as a function of *two* control parameters. We have varied the malonic acid concentration and the residence time τ (the ratio of the volume of the reactor to the total flow rate); the concentrations of the other input chemicals were held fixed. The instrumentation is described elsewhere [1,5].

Table 1 lists some of the observed periodic states, each of which consists of some combination of three basic patterns, 2^1, 1^1, and 2^2. The triplet (p, q, r) used to label each state is simply related to the number of times each of the basic patterns repeats in a single period: $p=b+c$, $q=b+a$, and $r=a+b+c$, where a is the number of times per period the patterns 2^1 repeats, b is the number of times the 1^1 pattern repeats, and r is the number of times the 2^2 pattern pattern repeats. For example, the state $2^1(1^1)^4 2^2$ in fig. 1b is labeled (5,5,6). Our choice of the relation of the integers (p, q, r) to the number of repetitions of the basic patterns is an arbitrary one; other sums and differences of the integers (a, b, c) would work just as well, but with the choice we have made we obtain exactly the same Farey triangle as discussed by Ostlund and Kim.

A Farey triangle constructed with the three basic states (0,1,1), (1,1,1), and (1,0,1) as the vertices is shown in fig. 2a. Successive levels of the Farey triangle are constructed as follows: the Farey mediant ($p+p'$, $q+q'$, $r+r'$) is placed at the midpoint of the hypotenuse that has the states (p, q, r) and (p', q', r') at its ends, and a line is drawn connecting this new state to the opposite vertex. This construction is continued *ad infinitum.* The observed states, which are indicated by the black dots in fig. 2a, *all* lie on the resultant Farey triangles. Thus, for example, the state (1,1,2) lies between the states (0,1,1) and (1,0,1), and the state (5,4,6) lies between (2,2,3) and (3,2,3). For a Farey triangle at any level the determinant whose rows consist of the vertices of the triangle has absolute magnitude unity. For example,

Table 1
Some of the periodic states observed in the Belousov–Zhabotinskii reaction in a well-stirred flow reactor as a function of τ and malonic acid concentration with the following concentrations held fixed: 0.00416 M $MnSO_4$, 1.5 M H_2SO_4 and 0.033 M $KBrO_3$. Each state is of the form $(2^1)^a(1^1)^b(2^2)^c$; the triplets (p, q, r) label the states in the Farey triangle, where $p=b+c$, $q=b+a$, and $r=a+b+c$ (see fig. 2). Each state occurs for some range in malonic acid concentration and τ; the values in the table correspond approximately to the middle of this range. Many states in addition to those listed were observed at intermediate values of the malonic acid concentration.

Malonic acid (M)	Residence time (s)	(p, q, r)
0.039	550	(0,1,1)
0.039	538	(1,2,2)
0.039	536	(2,3,3)
0.039	532	(3,4,4)
0.039	528	(4,5,5)
0.039	526	(1,1,1)
0.046	498	(2,2,3)
0.046	496	(3,3,4)
0.046	494	(5,5,6)
0.046	492	(7,7,8)
0.049	482	(5,4,6)
0.049	479	(4,3,5)
0.049	478	(6,4,7)
0.049	477	(7,4,8)
0.056	466	(3,2,4)
0.056	464	(4,2,5)
0.056	460	(6,3,7)
0.066	430	(1,4,5)
0.066	426	(1,2,3)
0.066	424	(1,1,2)
0.066	420	(1,0,1)

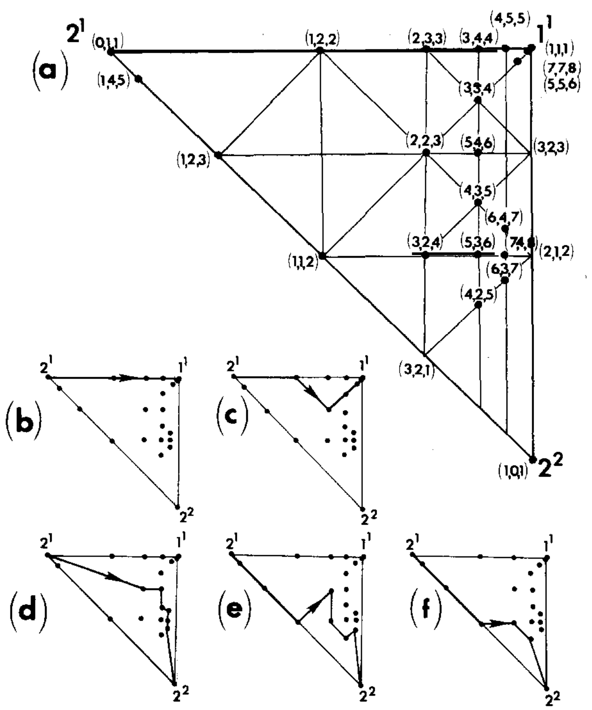

Fig. 2. (a) A Farey triangle with states (p, q, r) corresponding to the observed periodic states, which are indicated by the black dots; see table 1. The triangle was constructed starting with the basic states (0,1,1), (1,1,1), and (1,0,1) (corresponding to the waveforms 2^1, 1^1, and 2^2, respectively) at the vertices. The paths followed as a function of increasing τ are shown for the following malonic acid concentrations: (b) 0.039 M, (c) 0.046 M, (d) 0.049 M, (e) 0.056 M, (f) 0.066 M.

$$\begin{vmatrix} 2 & 2 & 3 \\ 5 & 4 & 6 \\ 4 & 3 & 5 \end{vmatrix} = -1 \,.$$

Figs. 2b–2f show the paths taken through the Farey triangle in measurements made as a function of τ for different fixed values of the malonic acid concentration. The triangle is systematically swept out by varying the two control parameters: roughly speaking, the path taken moves to the right with increasing τ and downward with increasing malonic acid concentration. Paths for different malonic acid concentrations do not cross.

All the states observed in this study were, within the experimental resolution, periodic. No hysteresis was discernible in the transitions between the different periodic states. However, evidence for the existence of intermediate higher period states was found when the control parameters were adjusted to be as close as possible to the values marking a transition from one state to another state; higher period state satisfying the Farey arithmetic were then observed, but only a few cycles would be observed before the system would drift into another state. Thus it seems fairly clear that higher period intermediate states exist over parameter ranges too narrow to be maintained with the resolution of the experiment.

Although the waveforms repeat fairly accurately from period to period, some variation in the amplitudes of the peaks of the time series was found (see fig. 1); presumably this variation is due to small fluctuations in the control parameters, but we cannot rule out the possibility of chaos on a small scale, as proposed by Richetti et al. [6].

Extensive recent studies of circle maps [7], which can be taken as Poincaré sections of a two-torus, have shown that frequency locking in maps can be organized by the Farey arithmetic that provides rational approximants of irrational numbers. Similarly, Kim and Ostlund show that frequency locking on a three-torus can be organized by the generalized Farey arithmetic that gives rational approximants for pairs of mutually irrational numbers. As we have shown, the Farey triangle of Kim and Ostlund describes our observations, but we should emphasize that we have no direct evidence for the existence of a three-torus – we have not observed quasiperiodicity either with two incommensurate frequencies (which on a three-torus would correspond to frequency locking of two of the three frequencies) or with three incommensurate frequencies. It is possible that the trajectories for our data do indeed lie on a three-torus, but that the control parameter range corresponding to quasiperiodicity is too small to be observable. Numerous experiments on the Belousov–Zhabotinskii reaction have yielded multipeaked periodic waveforms, but despite considerable efforts to find quasiperiodicity, it has been observed only in the studies of Roux, Argoul and coworkers [8]. Studies of models of the reaction by Barkley et al. [9] and Richetti et al. [6] have revealed regions of quasiperiodicity with two incommensurate frequencies, but the parameter ranges are small compared to the frequency-locked regions.

The self-similar structure of some periodic sequences in the Belousov–Zhabotinskii reaction can also be described with piecewise-linear maps, as first proposed by Tsuda [10]. Bagley et al. [11] have constructed a piecewise-linear map that yields a periodic sequence with the same symbolic dynamics that we reported previously (where our waveforms consisted of *two* basic patterns). Possibly a two-dimensional generalization of the map of Bagley et al. could yield a periodic sequence with the same symbolic dynamics as our sequence that has waveforms consisting of three basic patterns.

The Farley construction can be generalized further to describe our sequences with waveforms consisting of *four* basic patters, such as the state $2^3 2^2 (1^1)^2 1^2$ shown in fig. 1c. We have observed only six states of this type, but we find that they fit a three-dimensional Farey tree, a Farey *pyramid*, with vertices (p, q, r, s), where the integers are related to the number of repetitions per period of each of the basic patterns. It is possible that the periodic states with four basic patterns correspond to frequency locking on a four-torus.

In conclusion, the Farey triangle construction not only provides a natural compact organization of the data, but it also reveals the self-similar structure of the observed sequences. With the Farey triangle one can predict that, between any two states (p, q, r) and (p', q', r'), there will be the daughter state ($p+p'$, $q+q'$, $r+r'$) that will exist over a narrower parameter range than the parent states. This predictive power of the Farey triangle construction is corroborated by the experiments.

We thank S.H. Kim and S. Ostlund for helpful discussions. This work was supported by the Department of Energy, Office of Basic Energy Sciences.

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