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Chaoticity of some chemical attractors: a computer assisted proof

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In this paper we study dynamics of two chemical attractors. By means of computer assisted proof, we show that these chemical attractors are chaotic in terms of positive entropy. We prove that the fourth power of the Poincaré map derived from one chemical attractor and the second power of the Poincaré map derived from the other chemical attractor are semi-conjugate to the 2-shift map, therefore the entropies of the two Poincaré maps are not less than $\frac{1}{4}\log 2$ and $\frac{1}{2}\log 2$, respectively. The positivity of entropies of these two maps shows that the corresponding attractors are chaotic.

KEY WORDS: chemical attractors, horseshoe, Poincaré map, shift map

AMS subject classification: 34D15, 34D35, 37C10

1. Introduction

Chemical dynamics in a well-stirred reactor provides one of the most clear-cut examples of complex nonequilibrium behavior, since it can generate deterministic chaos from the intrinsic nonlinearities of the dynamics rather than from the spatial degrees of freedom. Since this form of chaos is amenable to a small number of macrovariables, one may reasonably expect that it constitutes an ideal case study for understanding the passage from microscopic to macroscopic behavior [1].

Chaotic dynamics is characterized by its sensitivity to initial conditions and is susceptible to external disturbances. Questions such as chaotic dynamics amplify internal noises and destroy the macroscopic description, and what

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the deterministic chemical chaos would become in the picture of a microscopic description beyond the phenomenological kinetics, are of much interest [2].

The study of chemically reacting systems through microscopic simulations is a subject of growing interest [3,4]. In this paper, we study dynamics of a class of chemical attractors. Different from the published papers that study chaotic chemical dynamics mainly by compute simulations, we show that these chemical attractors are chaotic by giving a compute-assisted proof based on horseshoe theory of dynamical systems, which is a powerful tool in studying chaos. Precisely, we prove the following facts: the entropies of the two Poincaré maps are not less than $\frac{1}{4}\log 2$ and $\frac{1}{2}\log 2$, respectively. The entropies of these two maps are positive, showing that the corresponding attractors are chaotic.

2. Two models of chemical system

2.1. Chemical system I

An interesting chemical system is established in [1], which is described by the following relations:

$$A_1 + X_1 \underset{k_{-1}}{\overset{k_1}{\rightleftarrows}} 2X_1,\ X_1 + Y_1 \xrightarrow{k_2} 2Y_1.$$

$$A_5 + Y_1 \xrightarrow{k_3} A_3,\ X_1 + Z_1 \xrightarrow{k_4} A_3,\ A_4 + Z_1 \underset{k_{-5}}{\overset{k_5}{\rightleftarrows}} 2Z_1 \tag{1}$$

The model exhibits a wide variety of dynamical behaviors including chaos. The model features two autocatalytic steps involving constituents X and Z, coupled through three other steps one of which is autocatalytic involving X, Z, and a third constituent Y. Assuming an ideal mixture and a well-stirred reactor, the macroscopic rate equations for the above system read as [1],

$$\begin{aligned} \dot{x}_1 &= \alpha_1 x_1 - k_{-1}x_1^2 - x_1 y_1 - x_1 z_1 \\ \dot{y}_1 &= x_1 y_1 - \alpha_5 y_1 \\ \dot{z}_1 &= \alpha_4 z_1 - x_1 z_1 - k_{-5} z_1^2 \end{aligned} \tag{2}$$

where x_1, y_1 and z_1 are the mole fractions of X_1, Y_1 and Z_1. The rate constants have been incorporated in the parameters α_1, α_5 and α_4 (e.g., $\alpha_1 = k_1(A_1)$). For more detailed discussions about this system see [1].

2.2. Chemical system II

In [2], the authors have studied a master equation for the chemical Lorenz system by means of ensemble stochastic simulations. The new model can be readily interpreted chemically on the base of mass action law as follows:

$$
\begin{array}{lll}
X_2 + Y_2 + Z_2 \xrightarrow{c_1} X_2 + 2Z_2, & 2X_2 \xrightarrow{c_6} P_2, & Y_2 \xrightarrow{c_{11}} P_6 \\
B_1 + X_2 + Y_2 \xrightarrow{c_2} 2X_2 + Y_2, & 2Y_2 \xrightarrow{c_7} P_3, & B_4 + Y_2 \xrightarrow{c_{12}} 2Y_2 \\
B_2 + X_2 + Y_2 \xrightarrow{c_3} X_2 + 2Y_2, & 2Z_2 \xrightarrow{c_8} P_4, & B_5 + Z_2 \xrightarrow{c_{13}} 2Z_2 \\
X_2 + Z_2 \xrightarrow{c_4} X_2 + P_1, & B_3 + X_2 \xrightarrow{c_9} 2X_2 & \\
Y_2 + Z_2 \xrightarrow{c_5} 2Y_2, & X_2 \xrightarrow{c_{10}} P_5 &
\end{array}
\tag{3}
$$

In the above reaction network, parameters $c_i (i=1, 2, \dots, 13)$ over the arrows are rate constants. Concentrations of species $B_i (i=1, 2, \dots, 5)$ and $P_i (i = 1, 2, \dots, 6)$ are assumed to be constant [2]. Given a well-stirred reactor and ideal mixture, the phenomenological rate equations of mass action law for the above reaction system read

$$
\begin{aligned}
\overset{\circ}{x}_2 &= c_2 x_2 y_2 - 2c_6 x_2^2 + c_9 x_2 - c_{10} x_2, \\
\overset{\circ}{y}_2 &= -c_1 x_2 y_2 z_2 + c_3 x_2 y_2 + c_5 y_2 z_2 - 2c_7 y_2^2 - c_{11} y_2 + c_{12} y_2, \\
\overset{\circ}{z}_2 &= c_1 x_2 y_2 z_2 - c_4 x_2 z_2 - c_5 y_2 z_2 - 2c_8 z_2^2 + c_{13} z_2^2,
\end{aligned}
\tag{4}
$$

where x_2, y_2 and z_2 are concentrations of species X_2, Y_2 and Z_2, respectively, and concentrations of $B_i (i = 1, 2, 5)$ have been incorporated into the rate constants c_2, c_3, c_9, c_{12}, and c_{13}. Equation (4) can exhibit various nonlinear behaviors qualitatively similar to the original Lorenz system [2]. Furthermore, as shown in this paper: the attractor of (4) has different topological structure from that of Lorenz system when the parameter c_1 be modified.

The purpose of this paper is to present a rigorous computer-assisted proof for chaotic behaviors of the attractors of (2) and (4) by virtue of a recent result of horseshoes theory in dynamical systems [5,6].

3. Review of a topological Horseshoe theorem

In this section, we recall a result on Horseshoes theory developed in [5], which is essential for rigorous verification of existence of chaos in the modified Chen's attractors discussed in this paper.

Let X be a metric space, D is a compact subset of X, and f: $D \to X$ is map satisfying the assumption that there exist m mutually disjoint subsets $D_1, \dots, D_m$ of D, the restriction of f to each D_i i.e., $f|D_i$ is continuous.

Definition 1. Let γ be a compact subset of D, such that for each $1 \leqslant i \leqslant m, \gamma_i = \gamma \cap D_i$ is nonempty and compact, then γ is called a connection with respect to $D_1, \dots, D_m$.

Let F be a family of connections γs with respect to $D_1, \dots, D_m$ satisfying the following property:

$$\gamma \in F \Rightarrow f(\gamma_i) \in F.$$

Then F is said to be a f-connected family with respect to $D_1, \dots, D_m$.

Theorem 2. Suppose that there exists a f-connected family F with respect to $D_1, \dots, D_m$. Then there exists a compact invariant set $K \subset D$, such that $f|K$ is semi-conjugate to m-shift

For the proof of this theorem, see [5].

Here the 'semi-conjugate to the m-shift' is conventionally defined in the following sense. If there exists a continuous and onto map

$$h : K \to \Sigma_m,$$

such that $h \circ f = \sigma \circ h$, then f is said to be semi-conjugate to σ, where σ is the m-shift (map) and $\sum_m$ is the space of symbolic sequences to be defined below. Let $S_m = \{1, \dots, m\}$ be the set of nonnegative successive integer from 1 to m. Let $\sum_m$ be the collection of all one-infinite sequences with their elements of S_m, i.e., every element s of $\sum_m$ is of the following form:

$$s = \{s_1, \dots, s_m, \dots\}, \quad s_i \in S_m.$$

Now consider another sequence $\bar{s}_i \in S_m$. The distance between s and $\bar{s}$ is defined as

$$d(s, \bar{s}) = \sum_{i=1}^{+\infty} \frac{1}{2^{|i|}} \frac{|s_i - \bar{s}_i|}{|s_i - \bar{s}_i| + 1} \tag{5}$$

with the distance defined as (5), $\sum_m$ is a metric space, and the m-shift map σ: $\sum_m \to \sum_m$ is defined as follows:

$$\sigma(s)_i = s_{i+1}, \quad s = \{s_1, \dots, s_m, \dots\}.$$

For the concept of topological entropy, the reader can refer [7,8]. We just recall the result stated in the lemma 3, which will be used in this paper.

Lemma 3. Let X be a compact metric space, and f: $X \to X$ a continuous map. If there exists an invariant set $\Lambda \subset X$ such that $f|\Lambda$ is semi-conjugate to the m-shift σ, then

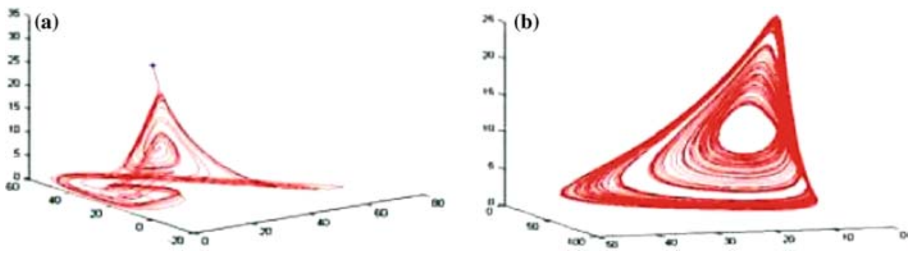

Figure 1. (a) The orbit of (2) for $\alpha_1 = 28.5$; (b) The orbit of (2) for $\alpha_1 = 30.1$.

$$h(f) \geqslant h(\sigma) = \log m,$$

where $h(f)$ denotes the entropy of the map f. In addition, for every positive integer k,

$$h(f^k) = kh(f).$$

A well-known fact is that if the entropy of continuous map is positive, then the map is chaotic [8].

4. Analyses of the two chemical systems

4.1. Dynamics of chemical system I

In [1], the author have claimed that chaotic attractor can be generated when $\alpha_1 = 30, \alpha_5 = 10$ and $\alpha_4 = 16.5, k_{-1} = 0.415, k_{-5} = 0.5$. Note that the parameter α_1 is an adjustable rate constant, the dynamics of (2) will be discussed for α_1 varying from 28.5 to 30.6, because the dynamics of (2) is trivial when $\alpha_1 < 28.5$ or $\alpha_1 > 30.6$. Let $\alpha_1 = 28.5$, we have the orbit as shown in figure 1(a). Computer simulations show that each orbit of (2) approaches to the stable equilibrium $(0, 0, 33)$ in the phase space for $\alpha_1 \in [28.5, 28.6159]$. As we increase α_1 up slowly, a strange attractor emerges. Computer calculations show that one of the Lyapunov exponents of (2) is positive for $\alpha_1 \in [28.616, 30.6]$, which is a numerical evidence that (2) is chaotic. In the next subsection, we present a proof by means of results in section 3.

4.2. Proof of chemical system I

In (2), let $\alpha_1 = 28.8, \alpha_5 = 10$ and $\alpha_4 = 16.5, k_{-1} = 0.415, k_{-5} = 0.5$, we have the attractor as shown in figure 2. Denote by $\varphi_1(x, t)$, the solution of (2) with initial condition x, i.e., $\varphi_1(x, 0)=x$. Consider the cross-section M_1 as shown in figure 1, with it's four vertices being $(0, 40, 5)$, $(10, 40, 5)$, $(10, 40, -2)$ and $(0, 40, -2)$.

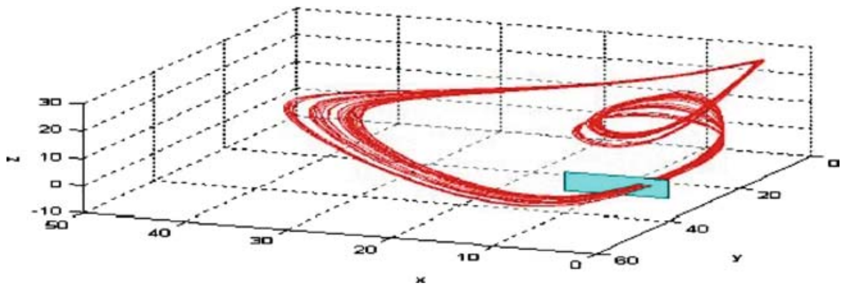

Figure 2. The attractor of (2) and cross-section.

We will study the corresponding Poincaré map on a subset of M_1. We select the quadrangle $|ABCD|$ with its vertices being $A(3.7447, 40, 1.0453)$, $B(3.7834, 40, 1.0629)$, $C(3.8236, 40, 1.0698)$ and $D(3.7948, 40, 1.055)$.

$$P : |ABCD| \to M_1$$

The map P is defined as follows: for each point $x \in |ABCD|$, $P(x)$ is the first return intersection point with M_1 under the flow with initial condition x. In order to find horseshoes, we consider $P_1 = P^4$.

Now we want to find two subsets of $|ABCD|$ as the subset D_1, D_2 defined in definition 1. By a great deal of computer simulation, we find two subset a_1 and a_2 of $|ABCD|$. The four vertices of a_1 are $(3.7815, 40, 1.0620)$, $(3.7834, 40, 1.0629)$, $(3.8236, 40, 1.0698)$ and $(3.8223, 40, 1.0691)$. The four vertexes of a_2 are $(3.7447, 40, 1.0453)$, $(3.7528, 40, 1.0490)$, $(3.8019, 40, 1.0586)$ and $(3.7948, 40, 1.0550)$.

The subsets a_1 and a_2 of $|ABCD|$ is shown in figure 3.

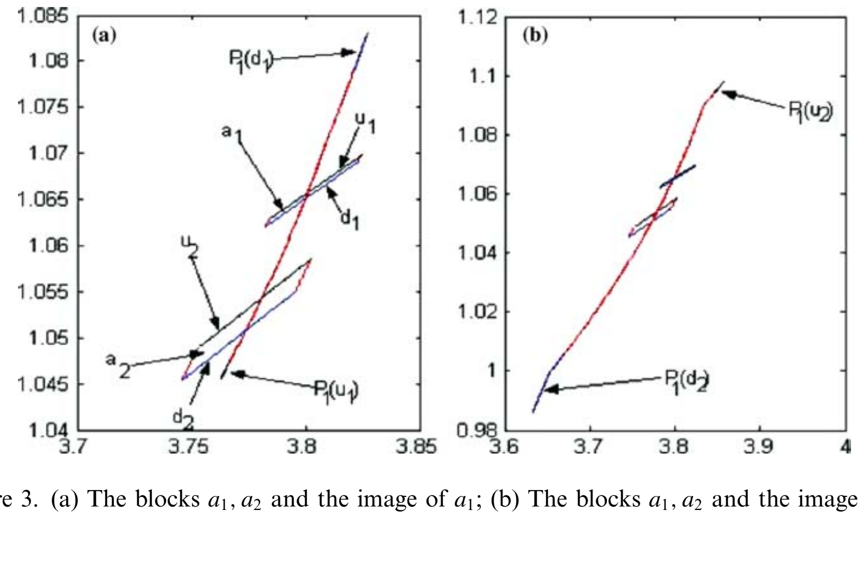

Figure 3. (a) The blocks a_1, a_2 and the image of a_1; (b) The blocks a_1, a_2 and the image of a_2.

Now let u_1 and u_2 be the upper sides of a_1 and a_2, respectively, and d_1 and d_2 be the low sides of a_1 and a_2, respectively. Then the computer computations show that $P_1(u_1)$ and $P_1(d_2)$ lie below the side d_2, $P_1(d_1)$ and $P_1(u_2)$ lie above the side u_1 as shown in figure 3.

It is easy to see from figure 3 that every line l lying in $|ABCD|$ and connecting the side AD and BC has nonempty connections with a_1 and a_2. Furthermore, $P_1(l \cap a_1)$ connects AD and BC from the above arguments, $P_1(l \cap a_2)$ also connects AD and BC. Therefore, it is easy to see, in view of definition 1, that there exists a P_1-family with respect to these two subsets a_1 and a_2 for the map P_1. It follows from Theorem 2 that there exists an invariant set K of $|ABCD|$, such that P_1 restricted to K is semi-conjugated to 2-shift dynamics. Let $h(P_1)$ be the entropy of the map P_1, it can be concluded from Lemma 3 that $h(P_1) = h(P^4) \geqslant h(\sigma) = \log 2$, consequently the entropy of the map P_1 is not less than $\frac{1}{4}\log 2$.

4.3. *A study on chemical system II*

In [2], the authors claimed that a deterministic chaotic trajectory can be generated when $c_1 = 0.88, c_2 = 10, c_3 = 29, c_4 = 100, c_5 = 100, c_6 = 5, c_7 = 0.5, c_8 = 1.3333, c_9 = 1000, c_{10} = 1000, c_{11} = 2900, c_{12} = 100, c_{13} = 10002.6667$. Note that the parameter c_1 is an adjustable rate constant, the dynamics (4) will be discussed when c_1 varies from 0.35 to 1.001, because the dynamics of (2) is trivial when $c_1 < 0.35$ or $c_1 > 1.001$.

In (4), let c_1=0.88, we have the attractor and equilibria as shown in figure 5. When we increase the parameter c_1, we first observed periodical trajectory in the phase space as illustrated in the following figure 4. There are two negative Lyapunov exponents and one zero Lyapunov exponents for the systems with $c_1 \in [0.35, 0.8650]$, it can be concluded that the observed periodical trajectory is a limit cycle when $c_1 \in [0.35, 0.8650]$. As we increase c_1 up slowly, the limit cycle disappears, and a strange attractor emerges. Computer calculations show that one of the Lyapunov exponents is positive for the systems with $c_1 \in [0.8655, 1.001]$. From compute simulation, we see that the chaotic attractor disappears when $c_1 \geqslant 1.002$.

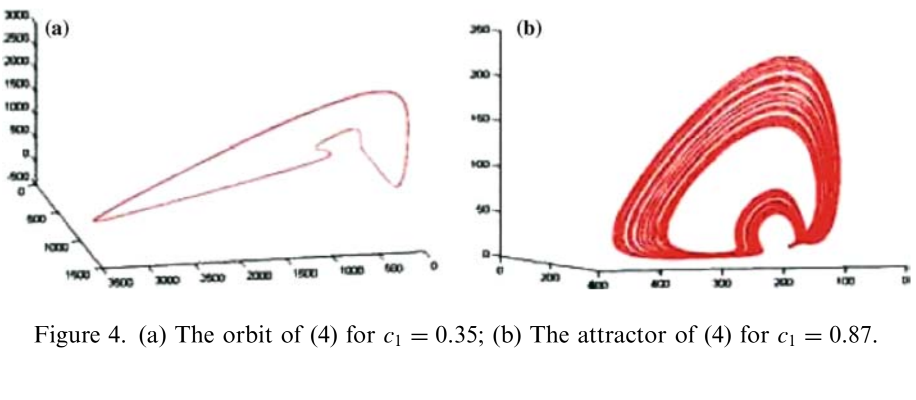

Figure 4. (a) The orbit of (4) for $c_1 = 0.35$; (b) The attractor of (4) for $c_1 = 0.87$.

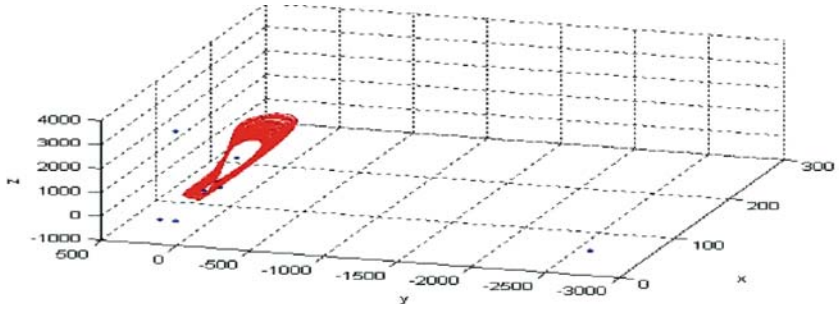

Figure 5. The attractor of (4) and its equilibria.

An important point to be stressed here is that although (4) is motivated by Lorenz system, the attractor of (4) has different topological structure from that of Lorenz system. The chemical system described by (4) have eight equilibria (figure 5). Among all of the equilibria, the equilibrium (100, 100, 0) is nearer to the attractor than others. The compute simulations show that the attractor lays out side of the open ball with center at (100, 100, 0) and radius being 1.1358. Therefore, contrary to the Lorenz system, the closure of this chaotic attractor does not contain any equilibrium.

4.4. *Proof of chemical system II*

Denote by $\varphi_2(x,t)$, the solution of (2) with initial condition x, i.e. $\varphi_2(x,0) = x$. Consider the cross-section M_2 as shown in figure 6, with it's four vertices being $(170, 200, 250)$, $(340, 200, 250)$, $(340, 200, 80)$ and $(170, 200, 80)$.

We will study the corresponding Poincaré map on a subset of M_2. We select the quadrangle $|EFGH|$ with its vertices being $E(220.2207, 200, 153.1022)$,

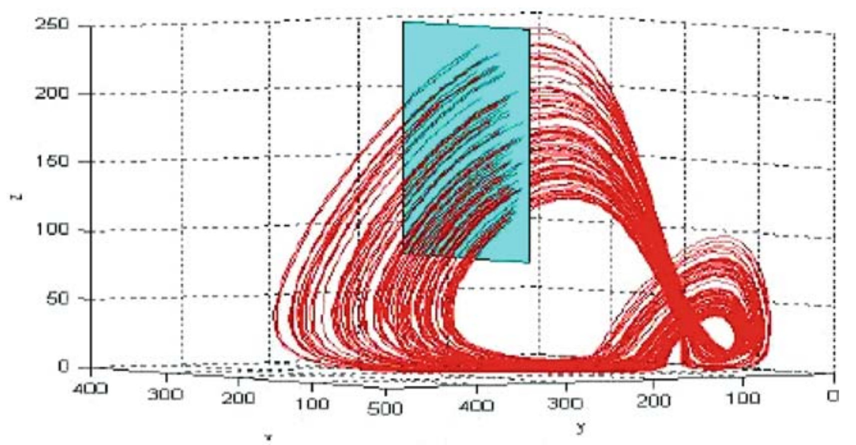

Figure 6. The attractor of (4) and its cross-section.

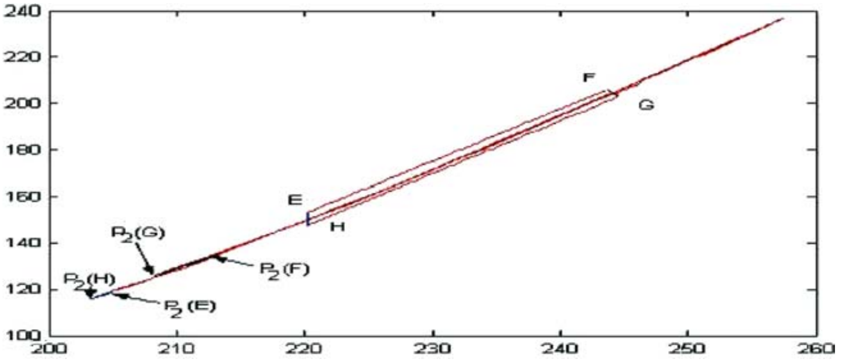

Figure 7. The quadrangle $|EFGH|$ and its image.

$F(243.6201, 200, 205.8623)$, $G(244.6257, 200, 203.1022)$ and H $(220.2207, 200, 147.6277)$.

$$\overline{P} : |EFGH| \to M_2$$

The map $\overline{P}$ is defined as follows: for each point $x \in |EFGH|$, $\overline{P}(x)$ is the first return intersection point with M_2 under the flow with initial condition x. In order to find horseshoes, we consider twice composition of the map $\overline{P}$, that is $\overline{P}^2$, let $P_2 = \overline{P}^2$.

Under this map P_2, the image of the quadrangle $|EFGH|$ is a very thin strip across $|EFGH|$ as shown in figure 7. Now we want to find two subsets of $|EFGH|$ as the subset D_1, D_2 defined in definition 1. By a great deal of computer simulation, we find two subsets b_1 and b_2 of $|EFGH|$. The four vertices of b_1 are (220.2207, 200, 153.1022), (229.58, 200, 174.21), (231.2, 200, 172.59) and (220.2207, 200, 147.6277). The four vertexes of b_2 are (230.17, 200, 175.53), (243.6201, 200, 205.8623), (244.6257, 200, 203.1022) and (231.81, 200, 173.98).

The subsets b_1 and b_2 of $|EFGH|$ is shown in figures 8 and 9.

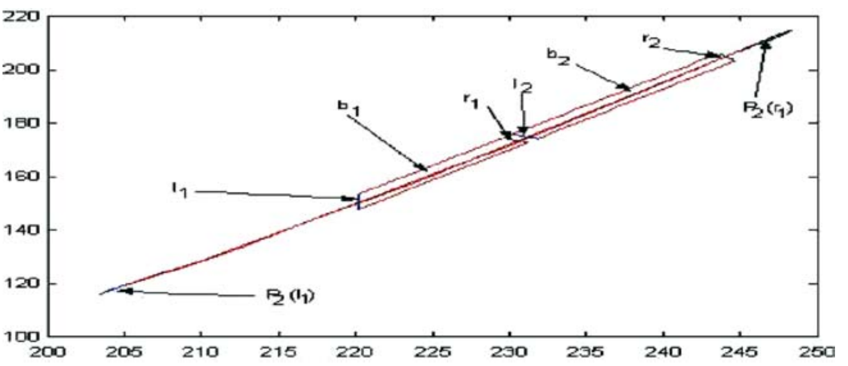

Figure 8. The blocks b_1 and b_2 and the image of b_1.

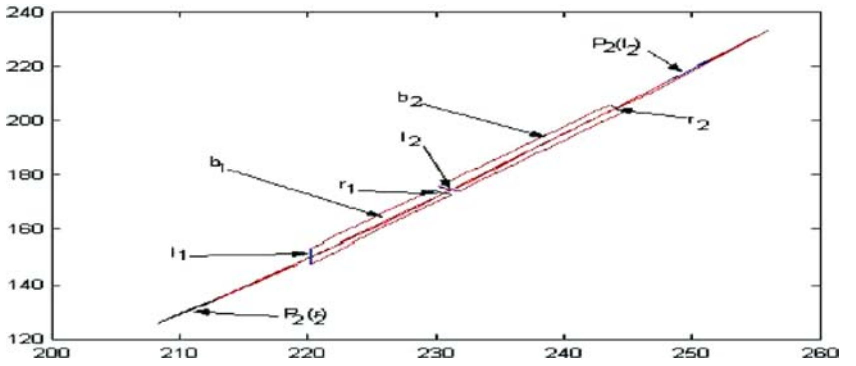

Figure 9. The blocks b_1 and b_2 and the image of b_2.

Now let l_1 and l_2 be the left sides of b_1 and b_2, respectively, and r_1 and r_2 be the low sides of b_1 and b_2, respectively. Then the computer computations show that $P_2(l_1)$ and $P_2(r_2)$ lie on the left side of l_1, $P_2(l_2)$ and $P_2(r_1)$ lie on the right side of r_2, as shown in figures 8 and 9.

It is easy to see from figures 8 and 9 that every line l lying in $|EFGH|$ and connecting the side l_1 and r_2 has nonempty connections with b_1 and b_2. Furthermore, $P_2(l \cap b_1)$ connects l_1 and r_2 from the above arguments, $P_2(l \cap b_2)$ also connects l_1 and r_2. Therefore, it is easy to see, in view of Definition 1, that there exists a P_2 -family with respect to these two subsets b_1 and b_2 for the map P_2. It follows from Theorem 2 that there exists an invariant set K of $|EFGH|$, such that P_2 restricted to K is semi-conjugated to 2-shift dynamics. Let $h(P_2)$ be the entropy of the map P_2, it can be concluded from Lemma 3 that $h(P_2) = h(\overline{p}^2) \geqslant h(\sigma) = \log 2$, consequently the entropy of the map P_2 is not less than $\frac{1}{2}\log 2$.

5. Conclusion

In this paper we study dynamics of two chemical attractors. We show that these chemical attractors are chaotic by means of computer assisted proof. We prove that the fourth power of the Poincaré map derived from the system I and the second power of the Poincaré map derived from the system II are semi-conjugate to the 2-shift map based on a newly established theorem 2 [5] on the existence of topological horseshoe and computer simulation. Therefore the entropies of the two Poincaré maps are not less than $\frac{1}{4}\log 2$ and $\frac{1}{2}\log 2$, respectively, showing that the corresponding attractors are chaotic.

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