

# Predmet:**Nove fizičkohemiske metode**

## Tema: Specifične metode ispitivanja dinamike složenih reakcionih sistema

Predavači: Ljiljana Kolar-Anić i Željko Čupić

### Sadržaj

#### I čas

1. Složeni reakcioni sistemi
2. Dinamičke strukture složenih reakcionih sistema i samoorganizacija neravnotežnih sistema
3. Modeliranje složenih reakcionih sistema

### Sadržaj II časa

- Analiza vremenskih serija
- Rekonstrukcija atraktora
- Poenkareovi preseci i mape
  - Cobweb dijagrami
  - Fiksna tačka

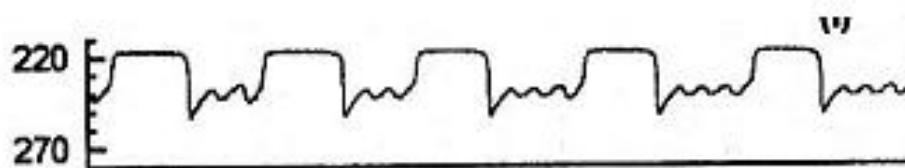
# Sadržaj II časa

- **Analiza vremenskih serija**
- Analiza atraktora
- Poenkareovi preseci i mape
  - Cobweb dijagrami
  - Fiksna tačka

# Vremenske serije

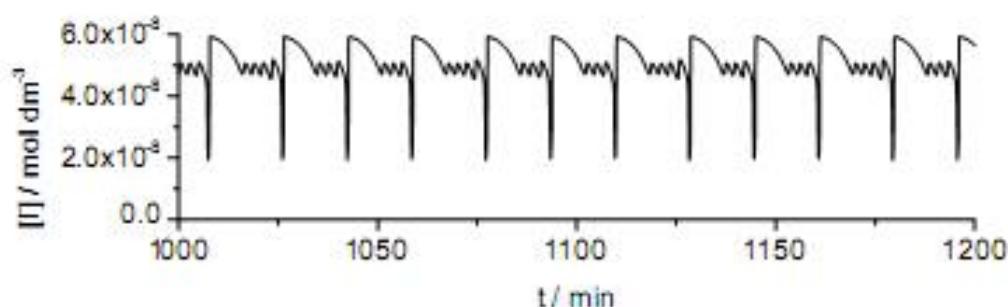
BL reakcije u dobro mešajućem **otvorenom** reaktoru.

Eksperimentalna ispitivanja



Vukojević, V.; Anić, S.; Kolar-Anić, Lj. *J. Phys. Chem. A* 2000, 104, 10731.

Numeričke simulacije



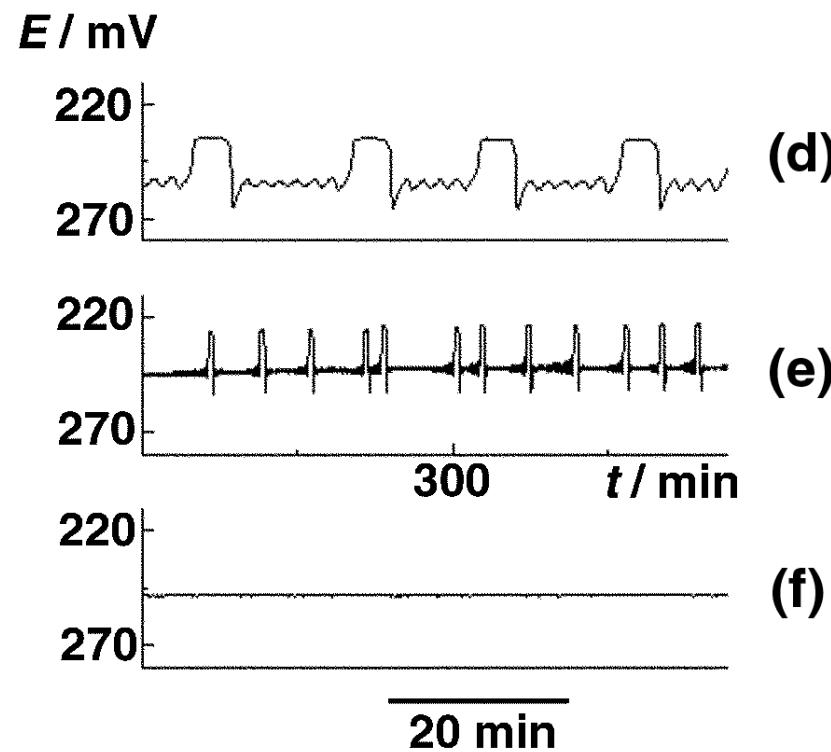
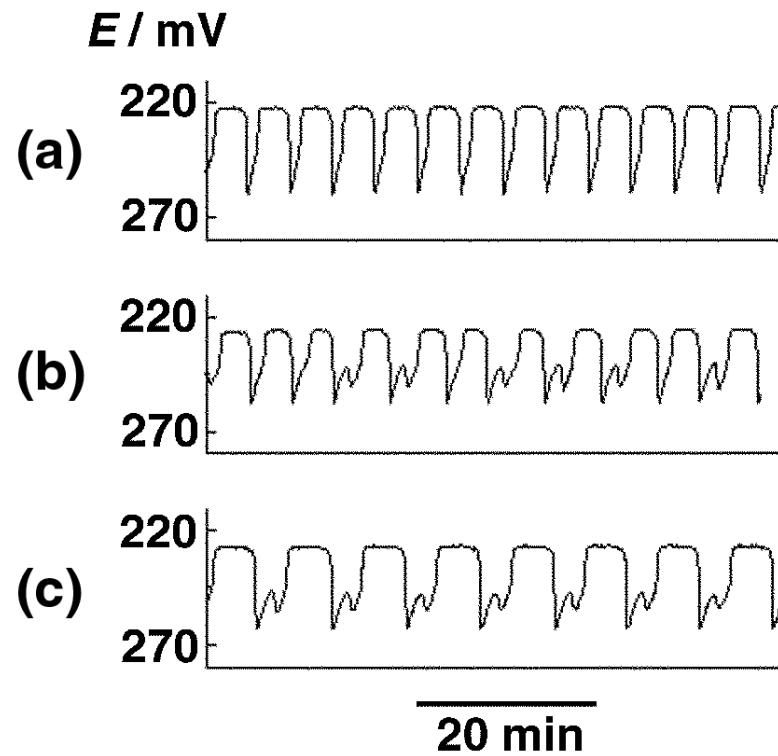
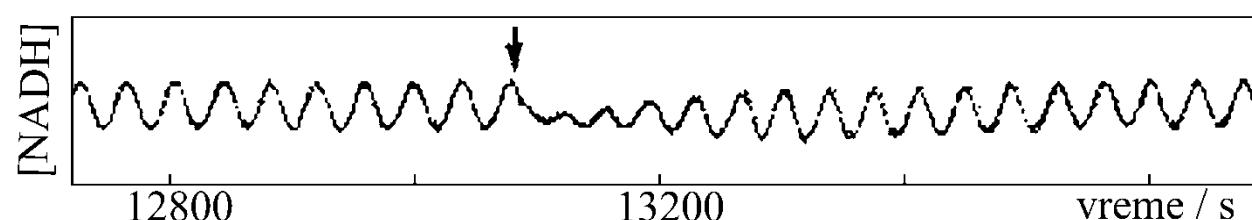
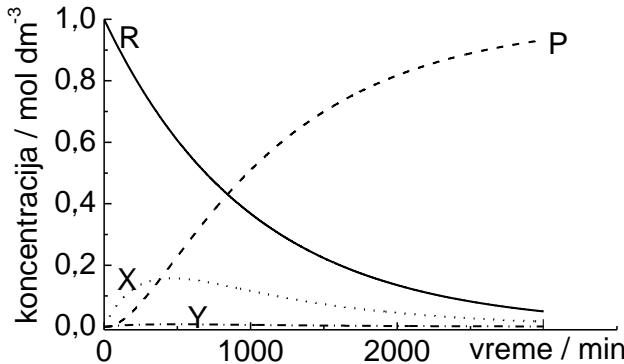
Lj. Kolar-Anić, T. Grozdić, Ž. Čupić, G. Schmitz, V. Vukojević, S. Anić,  
In *Selforganization in Nonequilibrium Systems*, SPCS, Beograd 2004. p.115

Time (min)	Reactor Temperature ©
0	26,486
0,3336	27,056
0,6671833	29,122
1,0007833	31,518
1,3343833	34,011
1,6679667	36,374
2,0015667	38,55
2,33515	40,033
2,66875	40,177
3,00235	39,638
3,3359333	39,27
3,6695333	39,354
4,0031333	39,635
4,3367167	39,829
4,6703167	39,866
5,0039	39,821
5,3375	39,806
5,6711	39,83
.....	.....

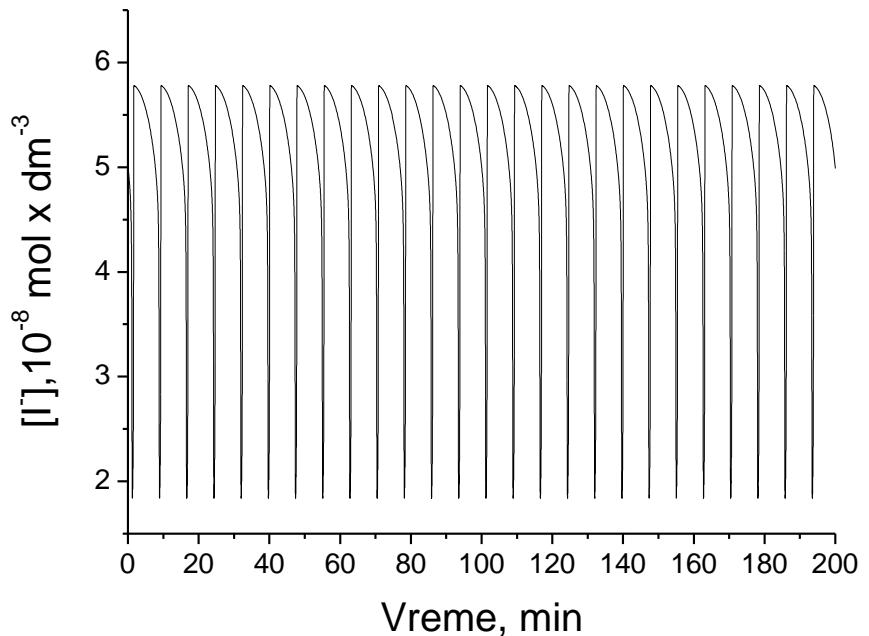
**Временске серије заправо представљају дигитални запис мереног сигнала са било ког лабораторијског инструмента који користимо за праћење стања испитиваног реакционог система.**

Reactor Temperature ©
26,486
27,056
29,122
31,518
34,011
36,374
38,55
40,033
40,177
39,638
39,27
39,354
39,635
39,829
39,866
39,821
39,806
39,83
.....

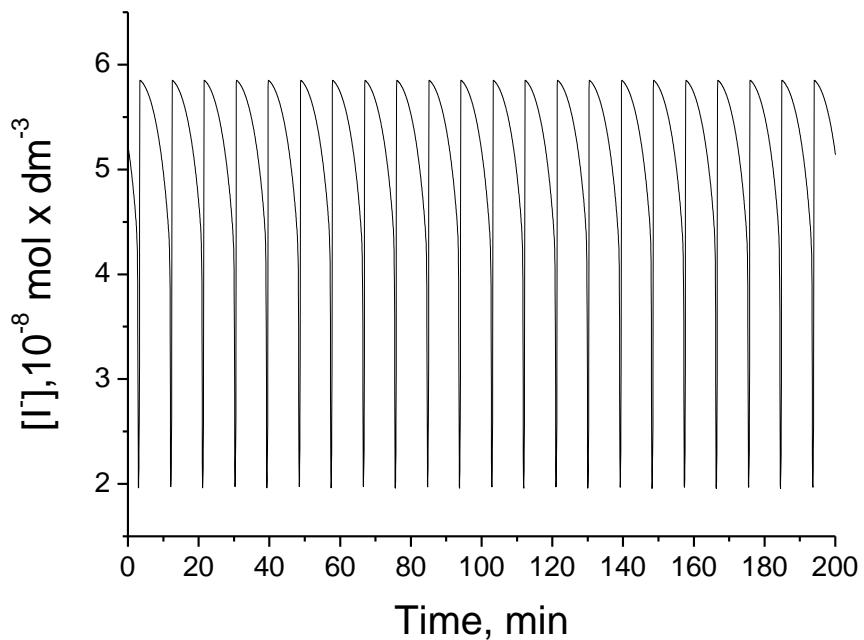
$$\Delta t = 0,3336 \text{ s} = \text{const}$$



a)



b)

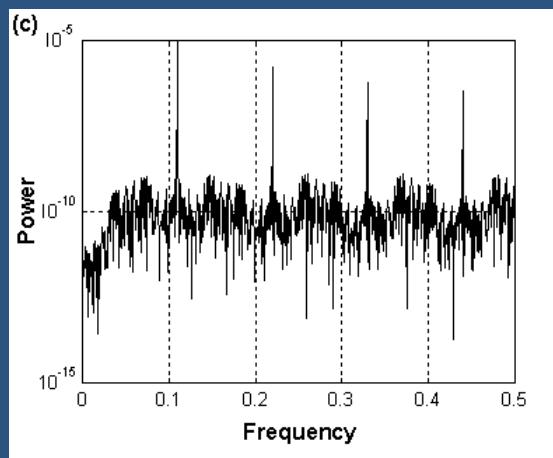
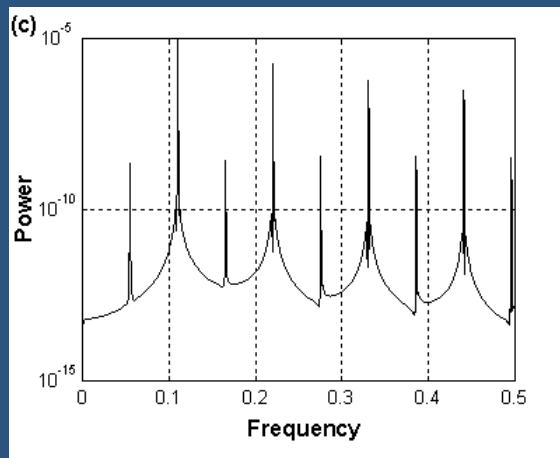
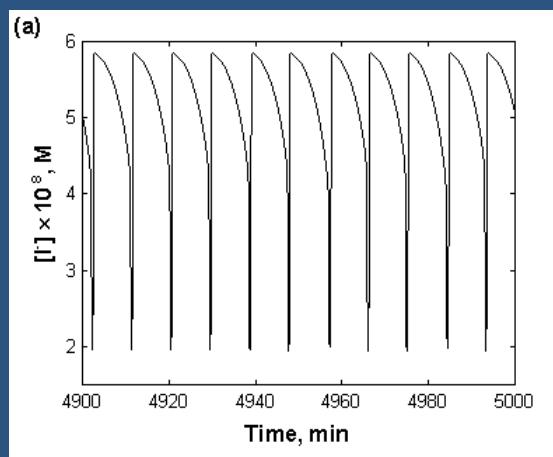
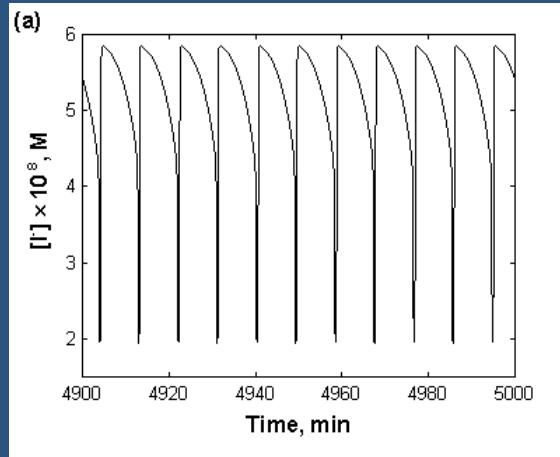


- a) Vremenska serija za protok  $j_0 = 4.824 \times 10^{-3} \text{ min}^{-1}$  – periodika  $(1^0)_2$   
b) vremenska serija za protok  $j_0 = 4.825 \times 10^{-3} \text{ min}^{-1}$  – haos tipa  $(1^0)_2$ .

# Spektri snage – metoda za analizu oscilatornih procesa

Spektar snage je kvadrat modula furijeove transformacije signala.

Prilikom udvajanja perioda dolazi do pojave subharmonika u spektru snage.



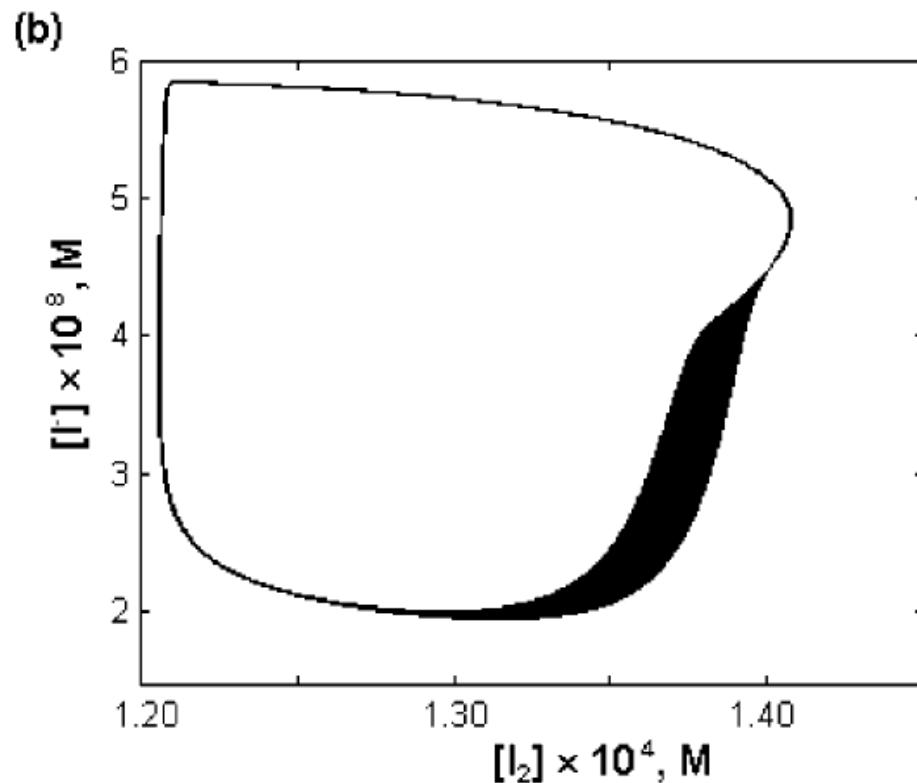
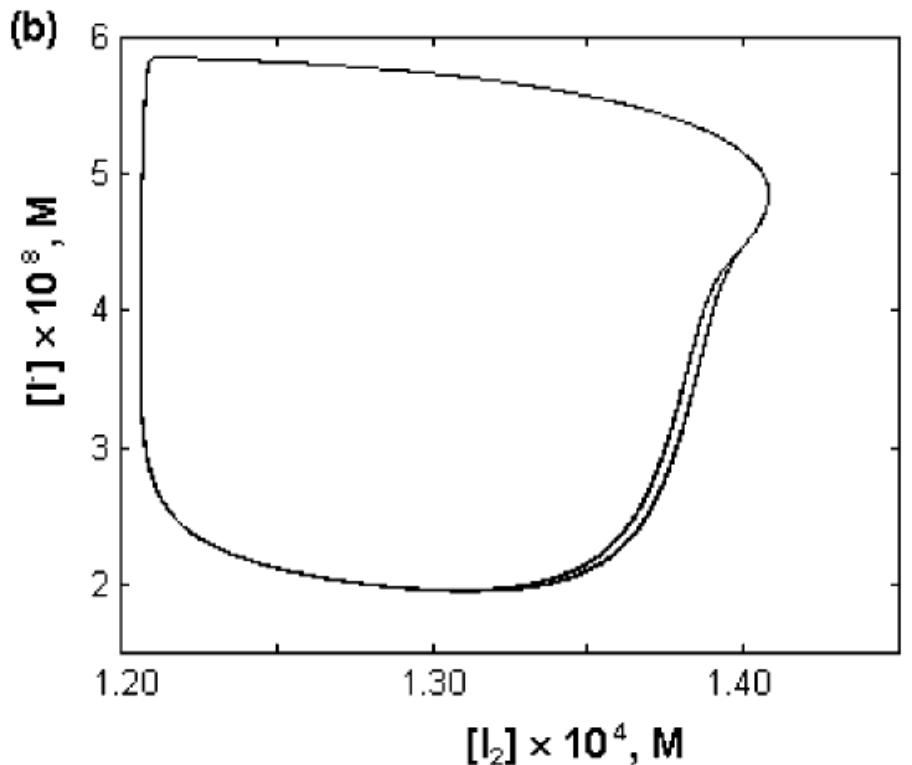
Slika 1

Slika 2

**Slika 1:**  
Period-2 oscilacije  
kada je  
 $j_0 = 4.824 \times 10^{-3} \text{ min}^{-1}$ ;  
(a) vremenska serija,  
i  
(c) spektar snage.

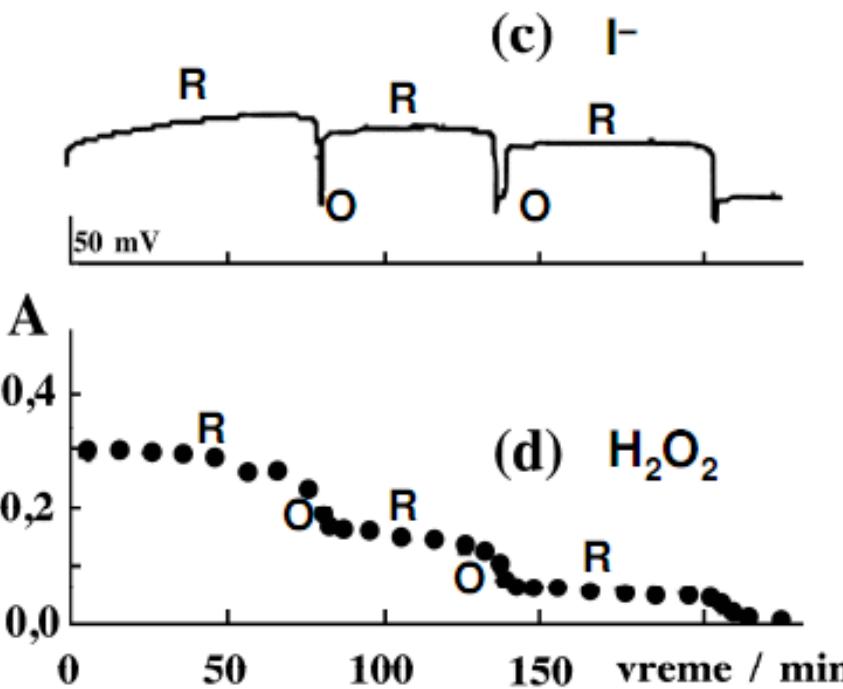
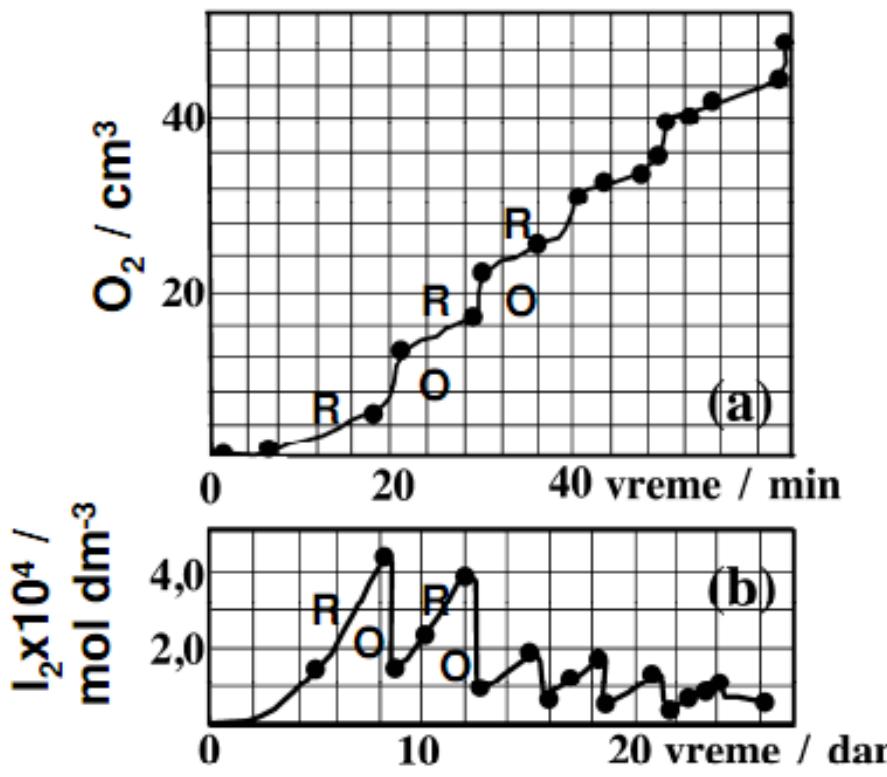
**Slika 2:** Haos  
Kada je  
 $j_0 = 4.825 \times 10^{-3} \text{ min}^{-1}$ ;  
(a) vremenska serija,  
i  
(c) spektar snage.

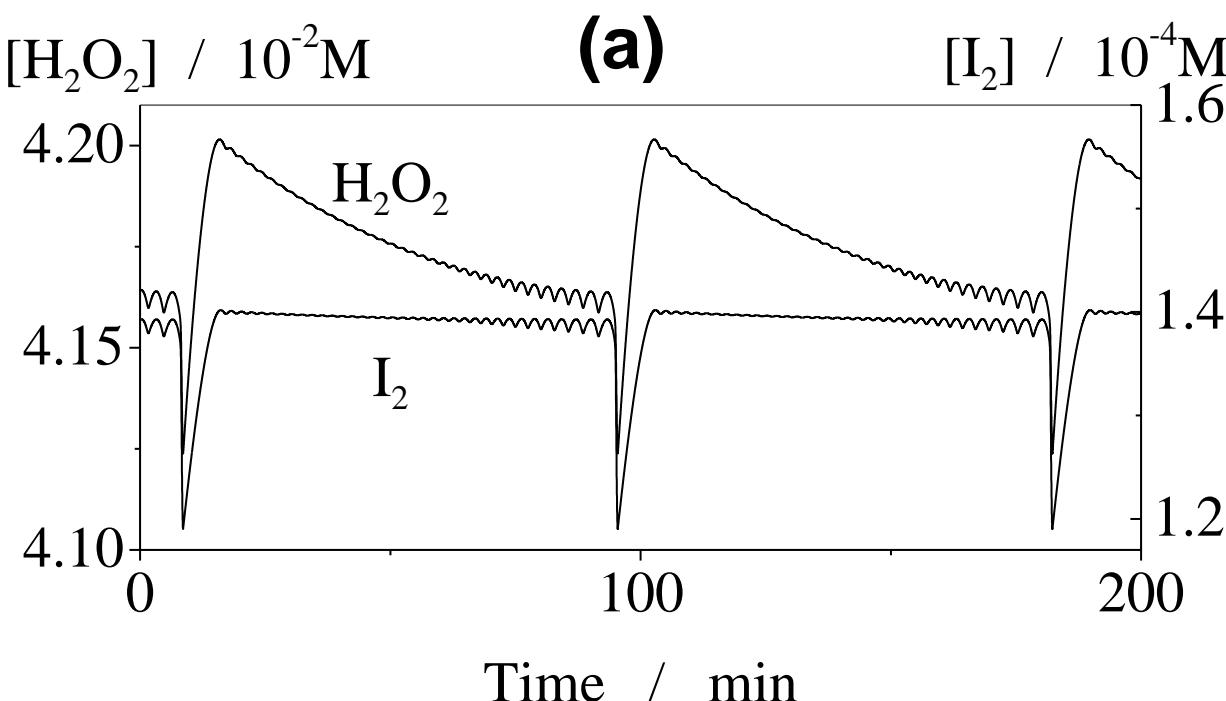
Guy Schmitz, Ljiljana Kolar-Anić,  
Slobodan Anić, Tomislav Grozdić,  
Vladana Vukojević  
*J. Phys. Chem. A*,  
110 (2006) 10361-10368.



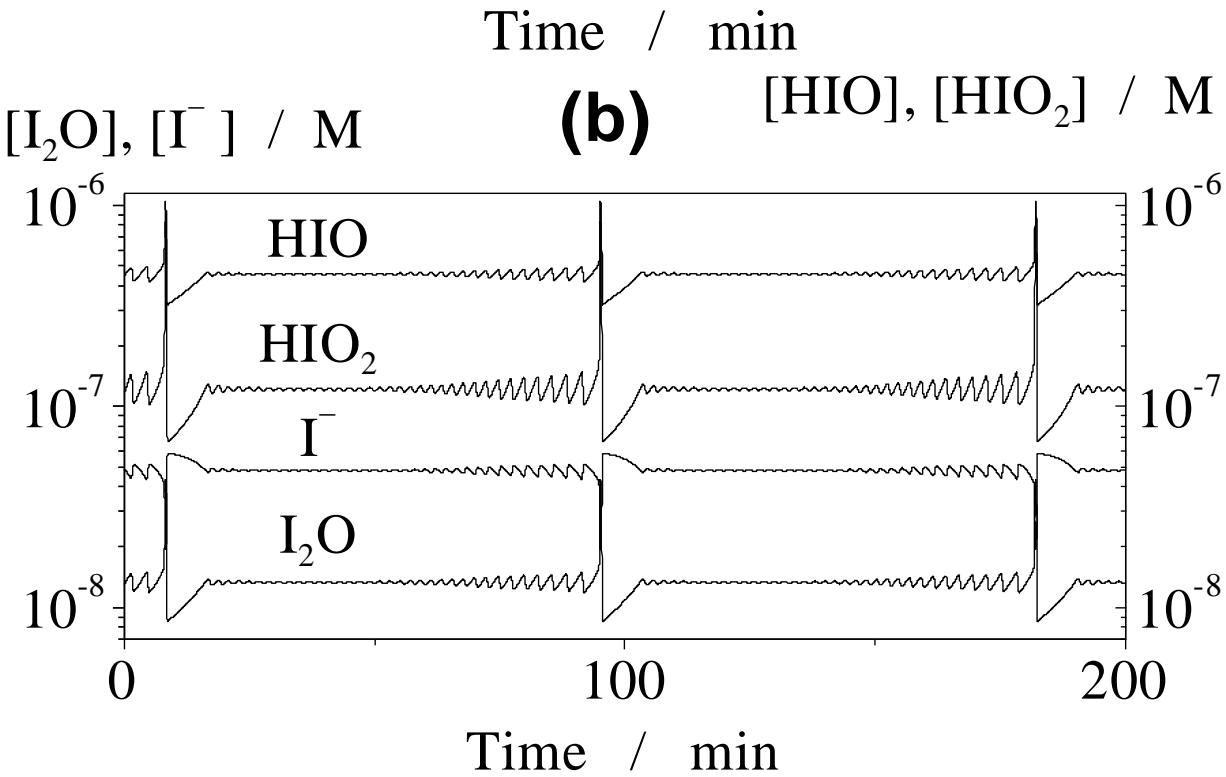
- a) Atraktor koji odgovara protoku  $j_0=4.824 \times 10^{-3} \text{ min}^{-1}$  – periodika  $(1^0)_2$  i  
b) Atraktor koji odgovara protoku  $j_0=4.825 \times 10^{-3} \text{ min}^{-1}$  – haos tipa  $(1^0)_2$ .

# Eksperimentalna merenja su ograničena na nekoliko vrsta

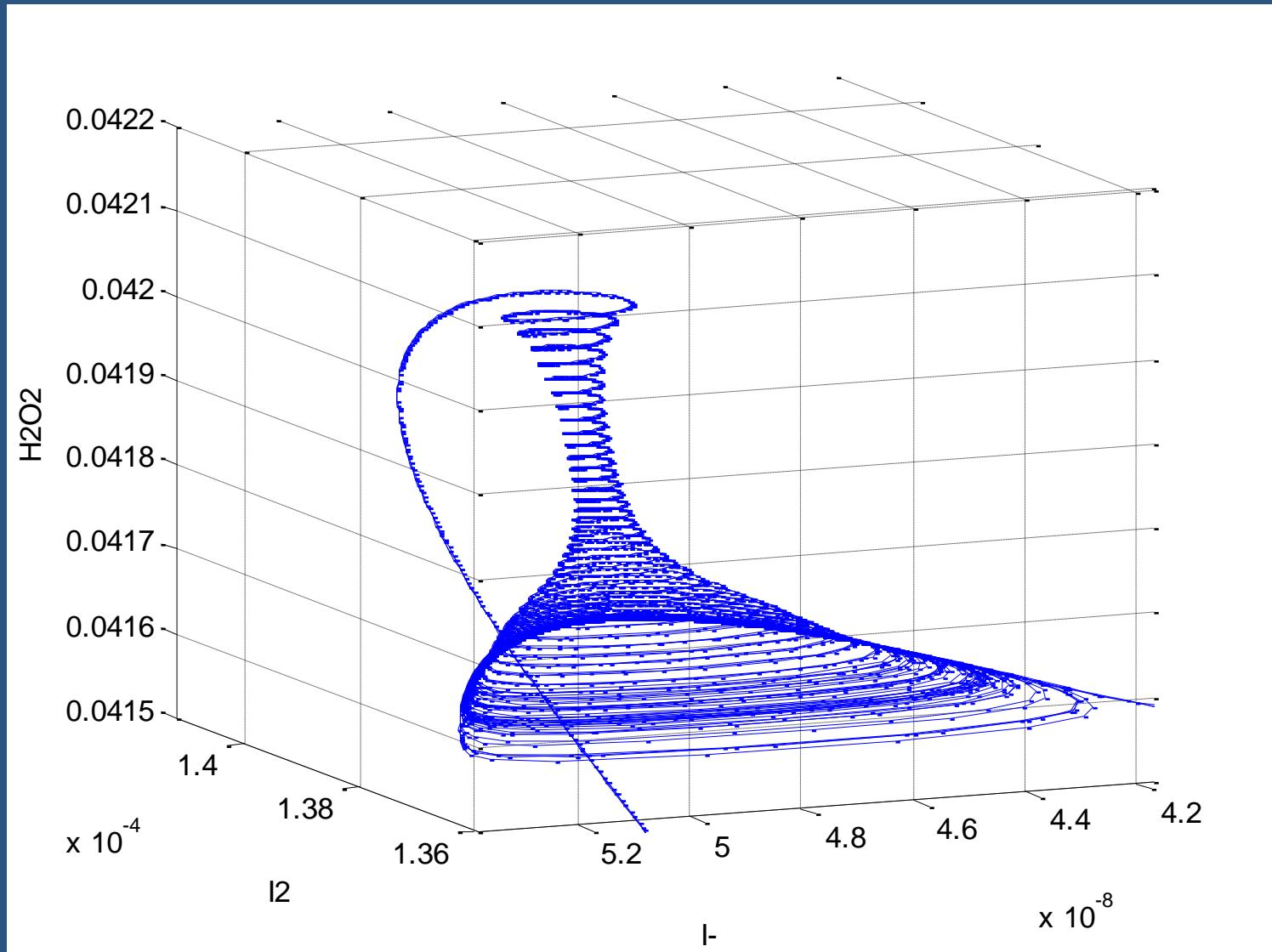




Za opisivanje stanja sistema u proizvoljnom trenutku neophodno je poznavanje koncentracija svih reaktanata i još većeg broja intermedijera



# Trajektorija u koncentracionom faznom prostoru



# Sadržaj II časa

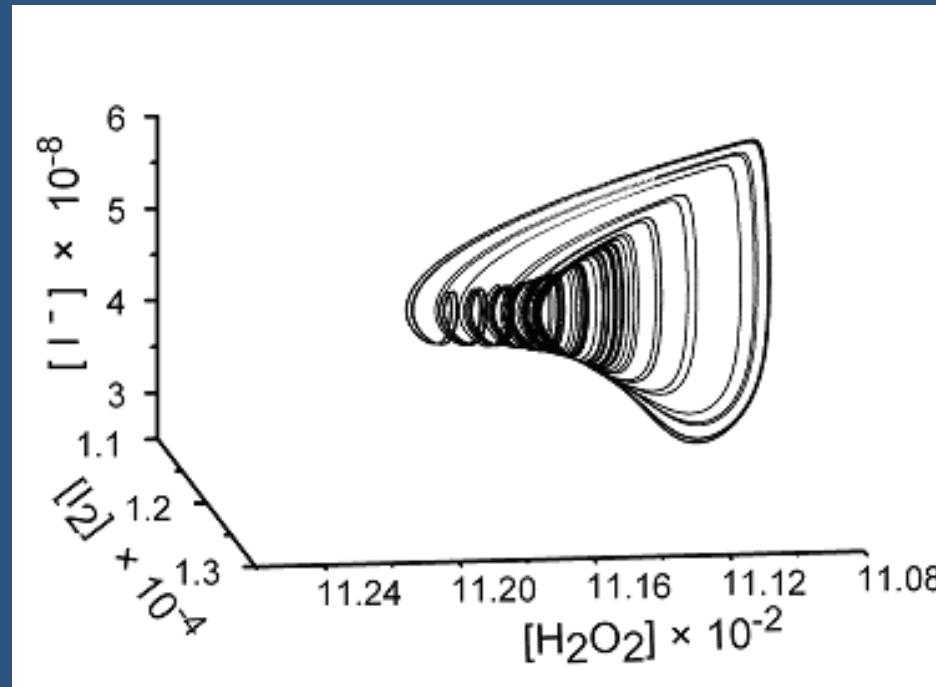
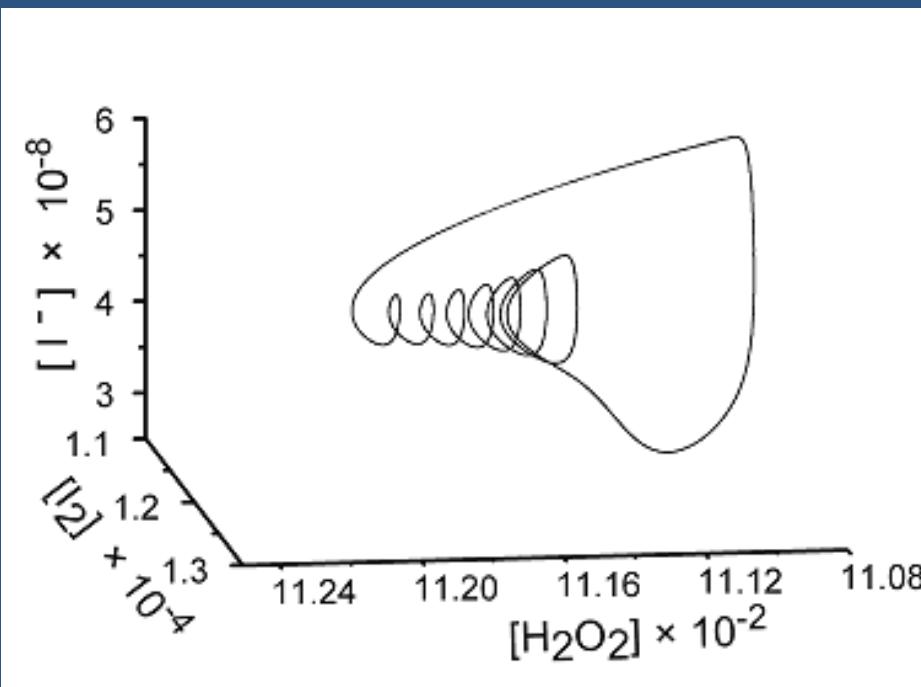
- Analiza vremenskih serija
  - **Analiza atraktora**
- Poenkareovi preseci i mape
  - Cobweb dijagrami
  - Fiksna tačka

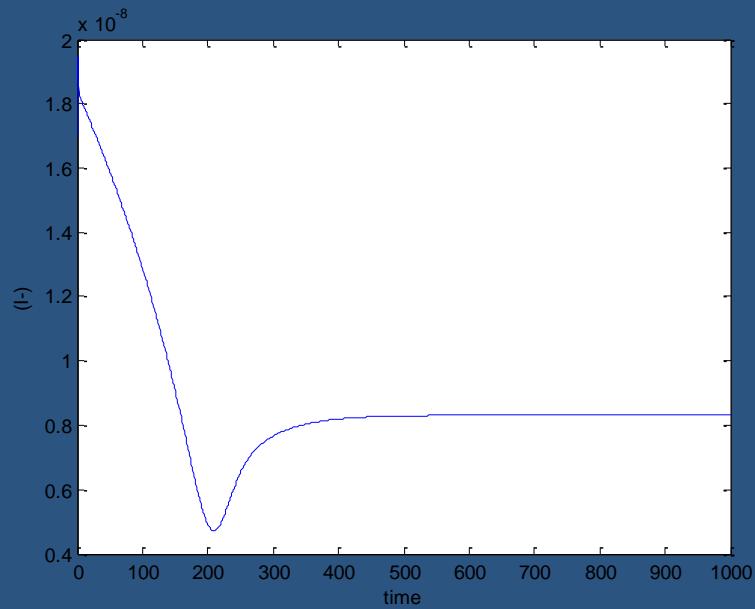
# Fazni prostor i atraktor

Atraktor je trajektorija dinamičkog sistema u faznom prostoru posle prolaska tranzijentnog perioda.

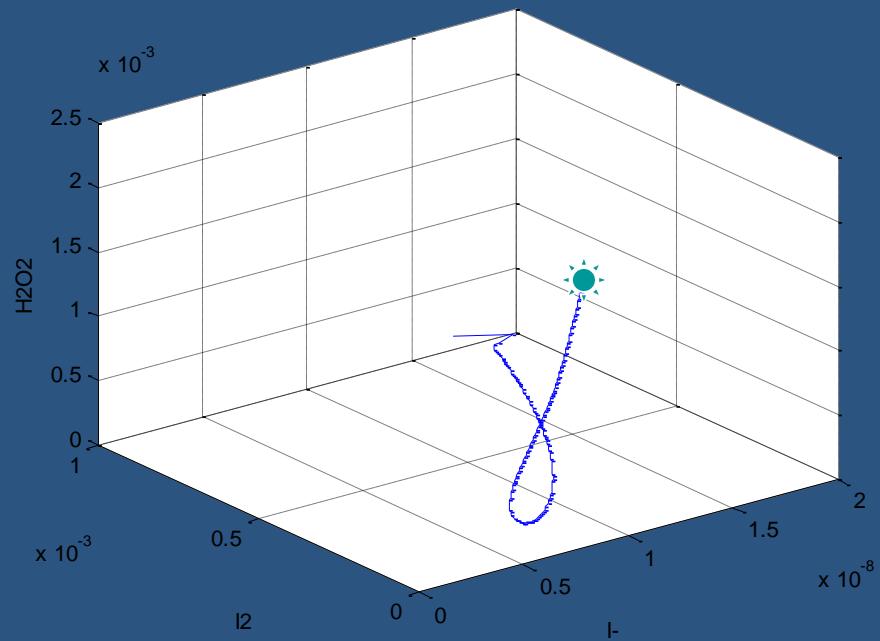
Periodične promene u vremenu su posledica kretanja dinamičkog sistema po zatvorenoj putanji u faznom prostoru.

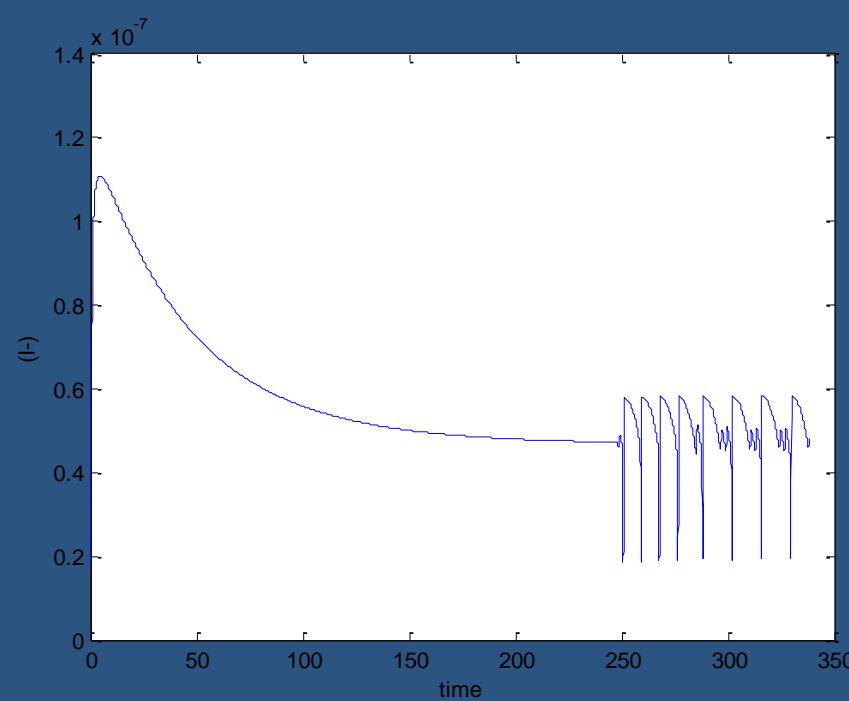
Haotičnoj dinamici odgovara otvorena putanja po ograničenom delu faznog prostora



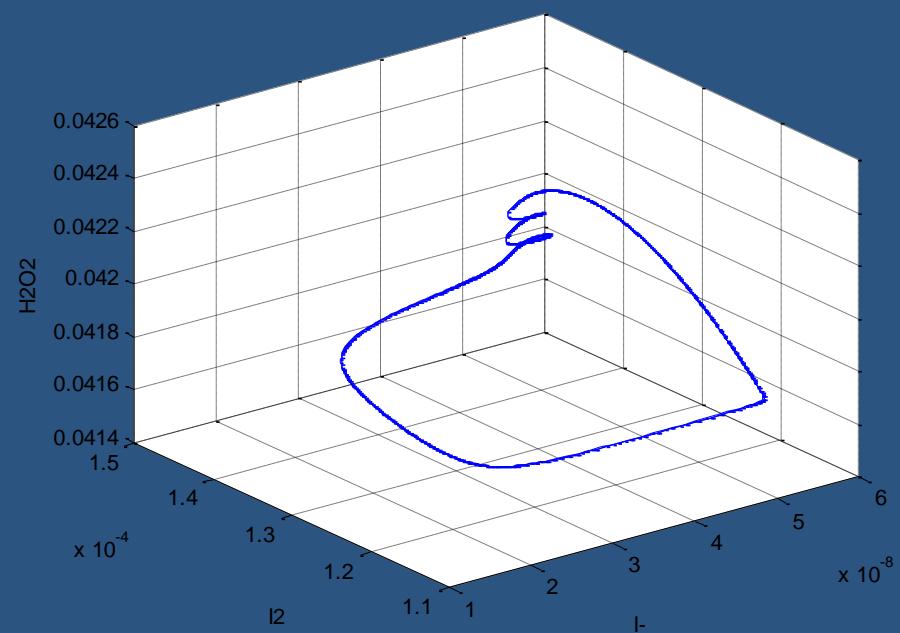
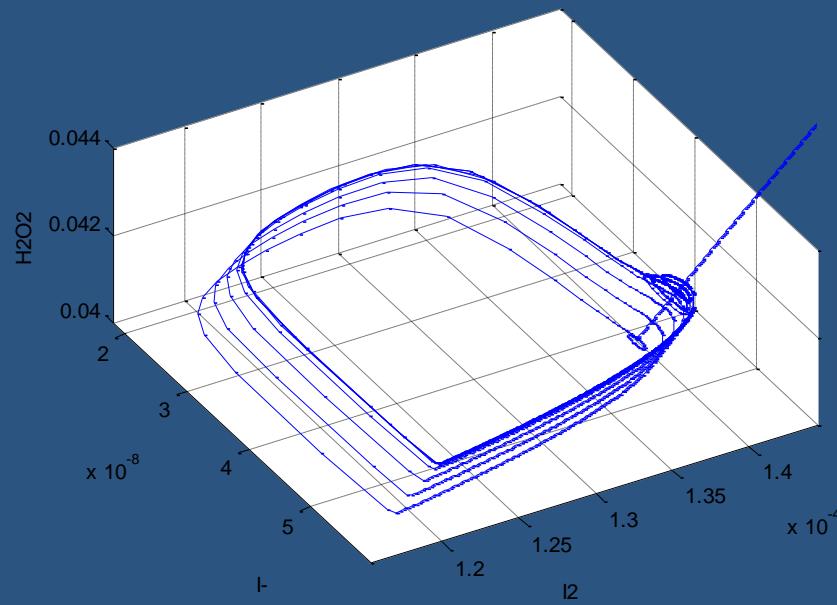


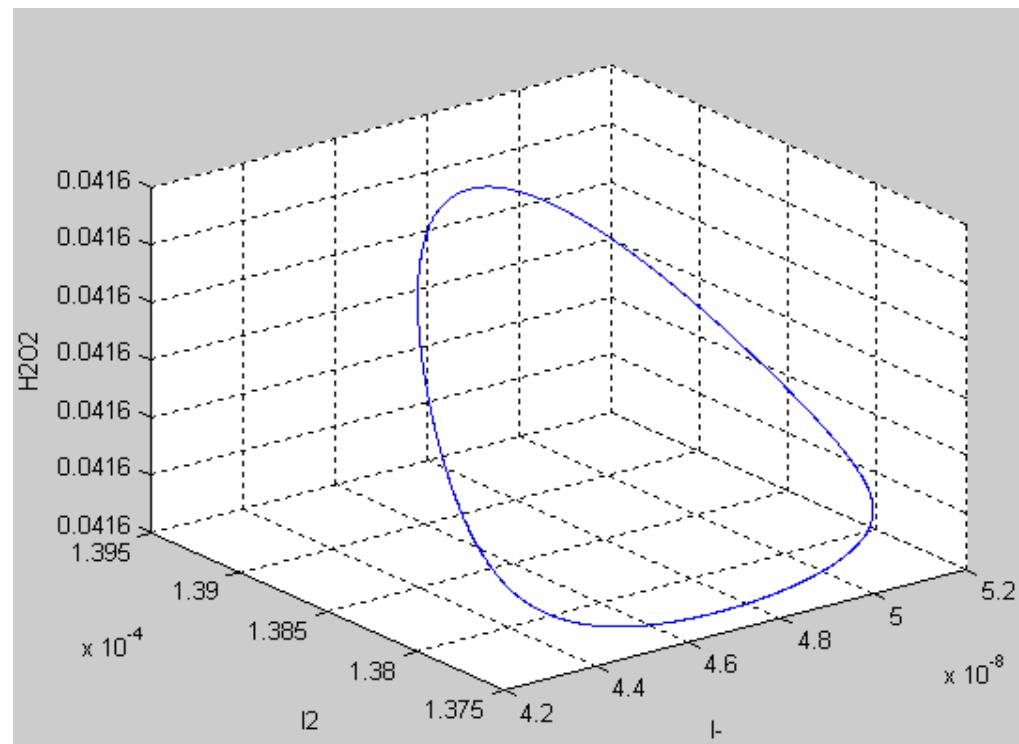
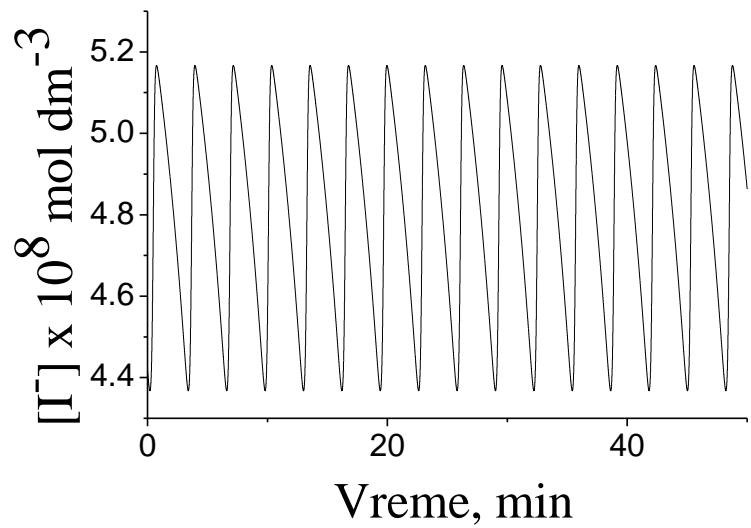
Slučaj 1 (stabilnost): Atraktor je  
**STACIONARNO STANJE**

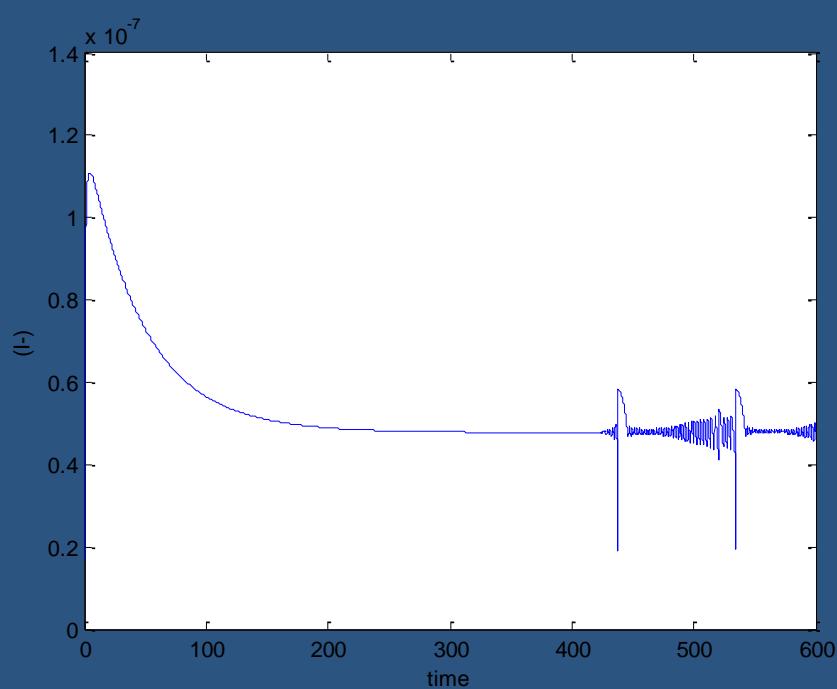




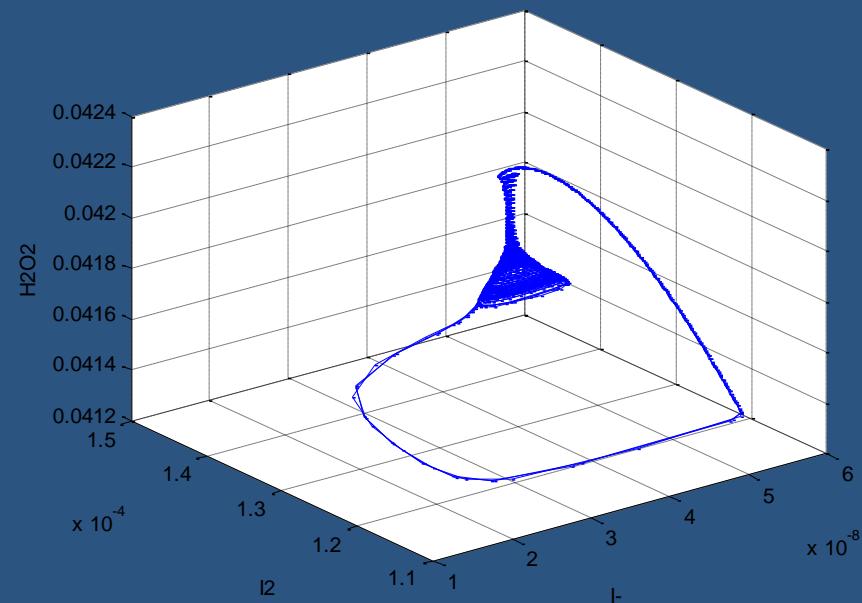
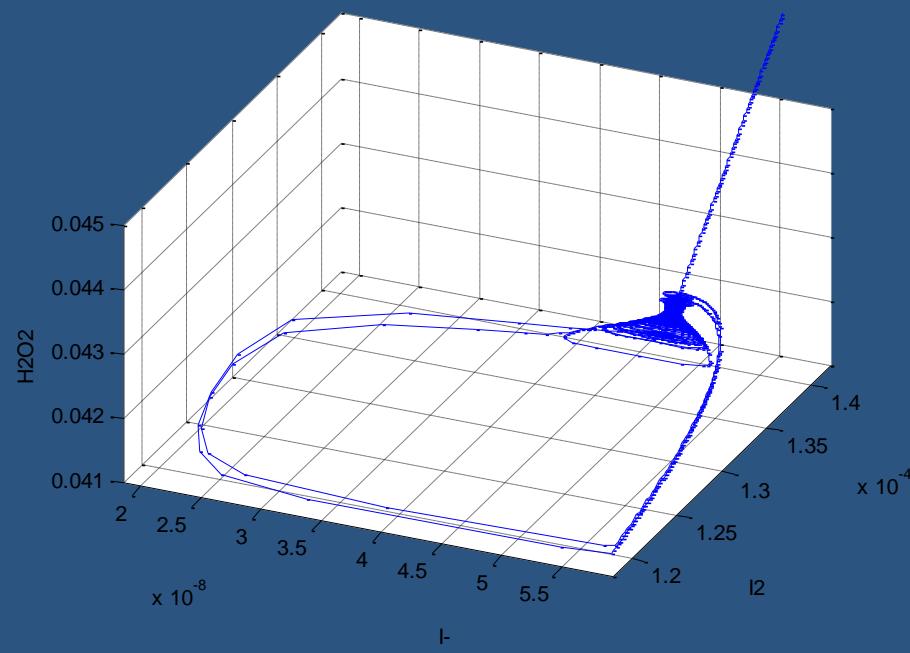
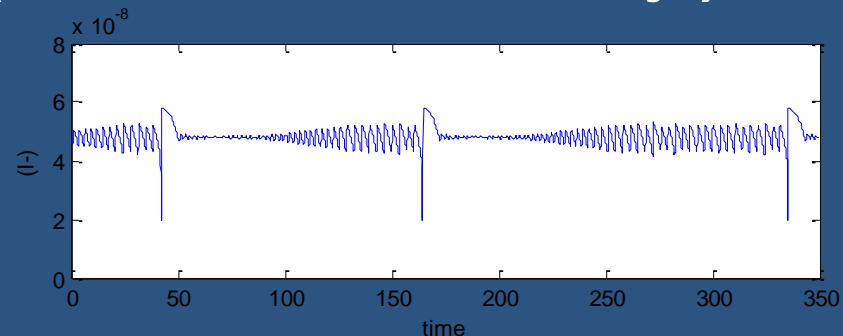
## Slučaj 2: Atraktor je GRANIČNI KRUG







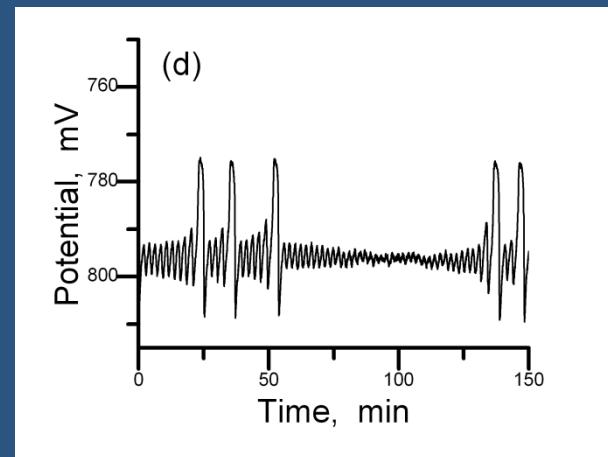
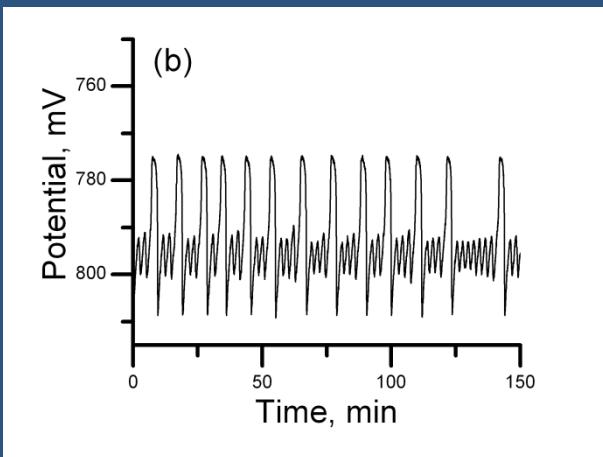
## Slučaj 3 (haos): Atraktor je ČUDNI ATRAKTOR (fraktal – otvorena linija)



Vremenska serija

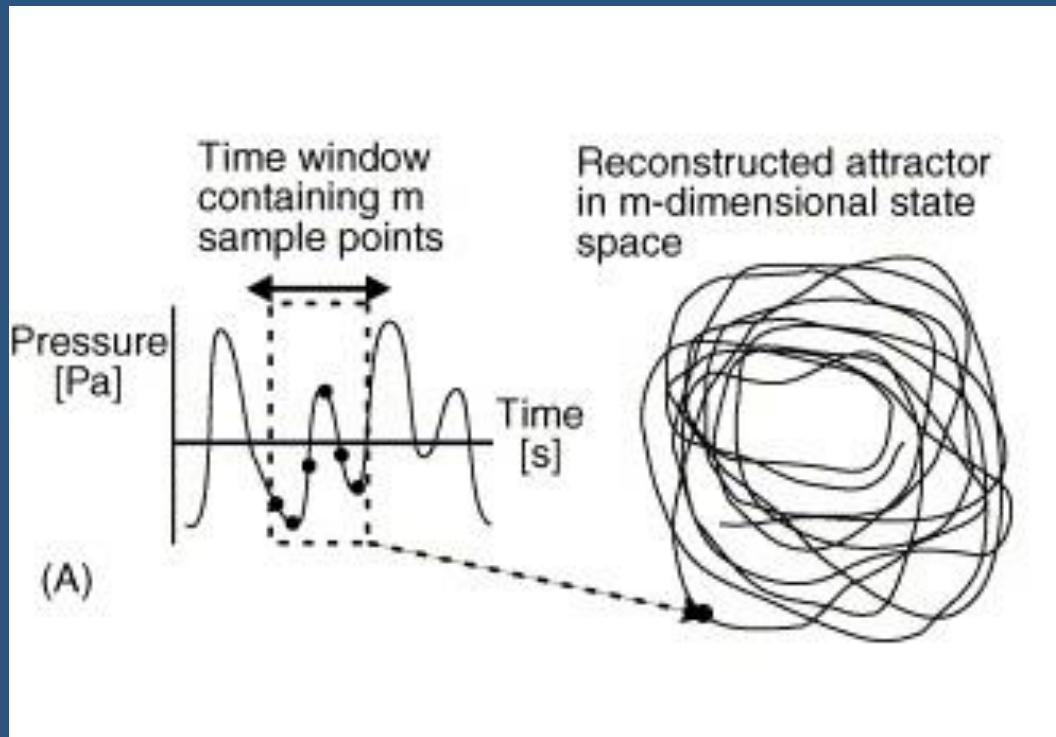


Atraktor u faznom prostoru



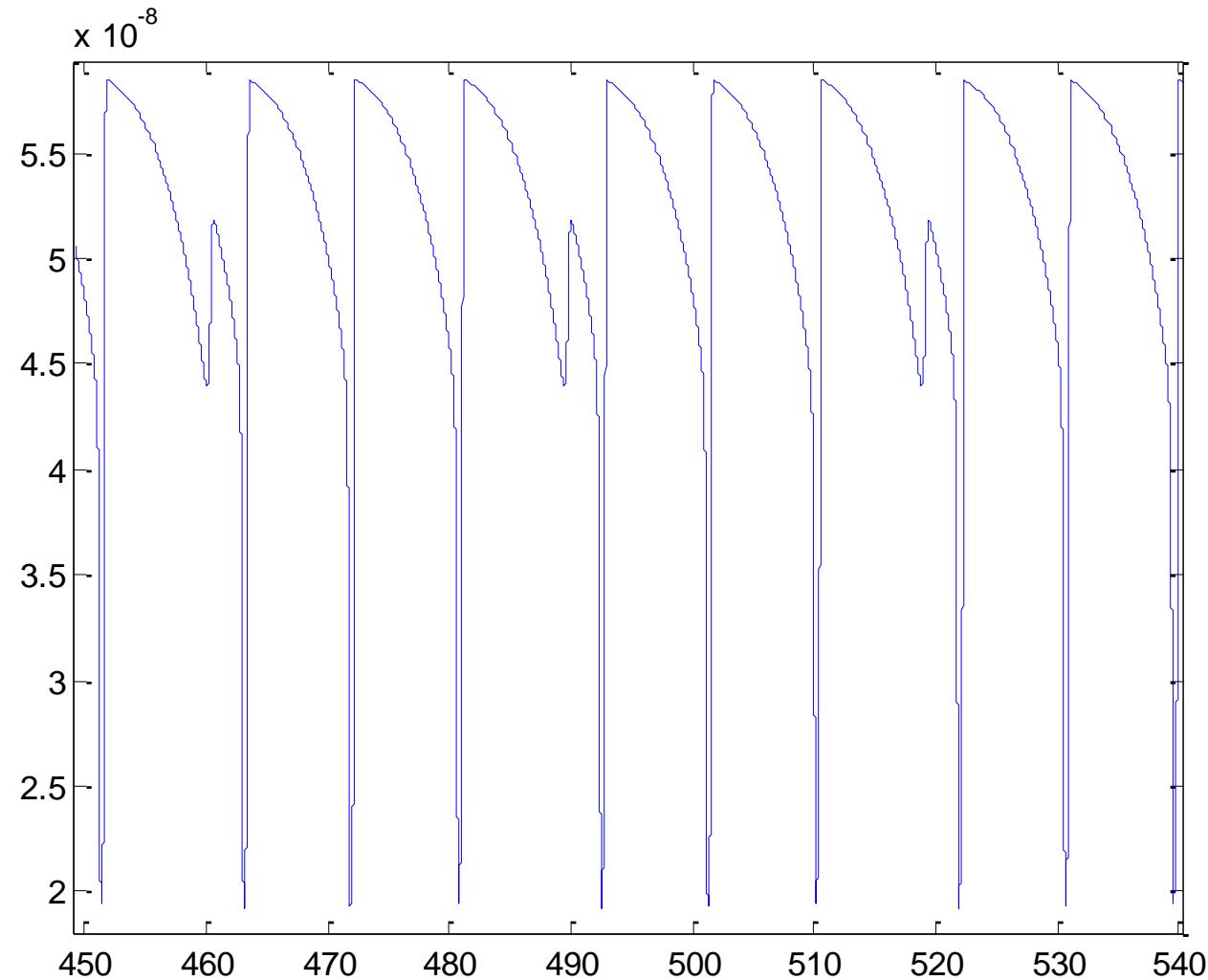
# Rekonstrukcija atraktora

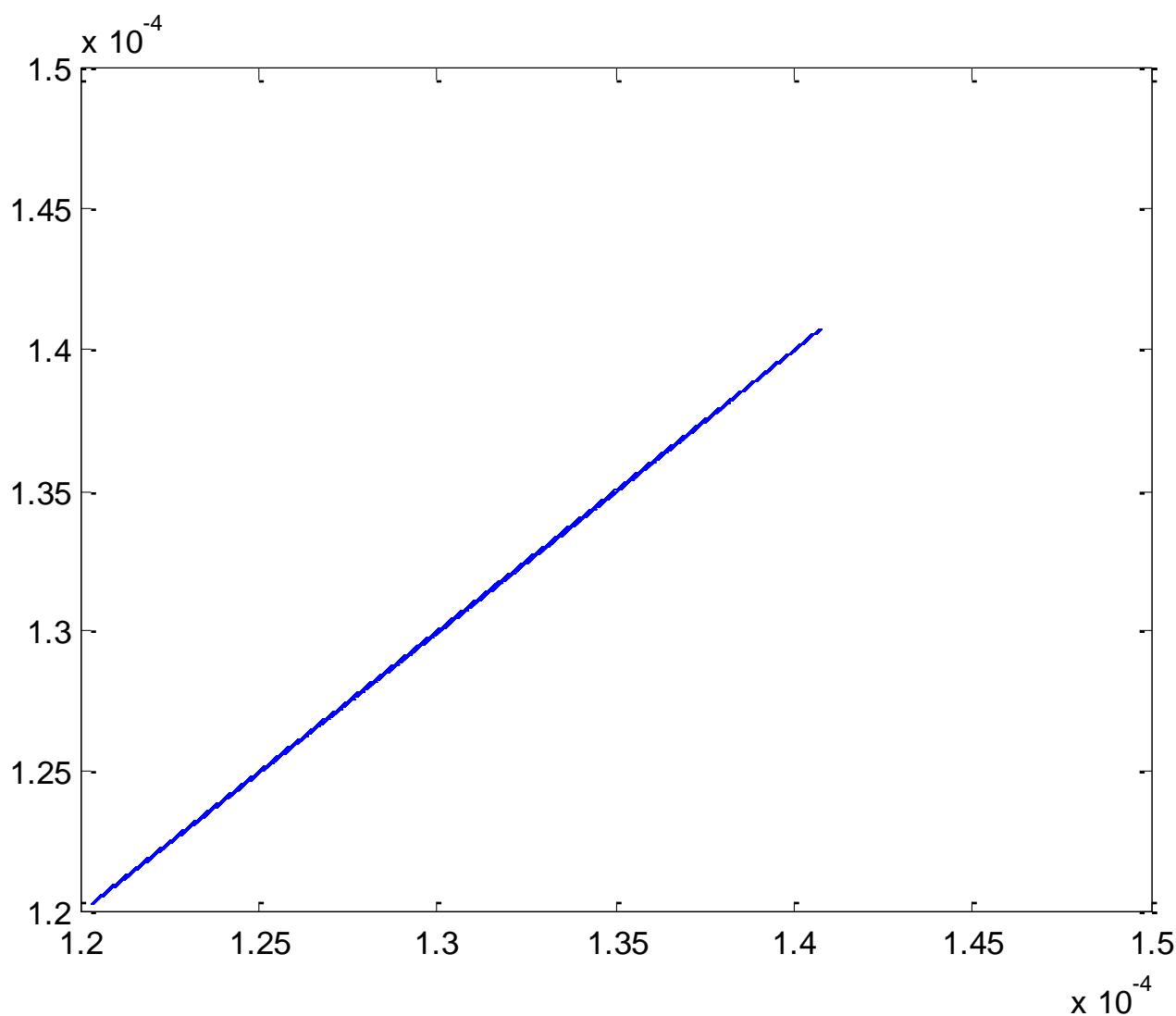
Floris Takens je dokazao da umesto  $2n+1$  generičkih signala, za prekrivanje  $n$ -dimenzionalnog atraktora može biti dovoljna konstrukcija sa vremenskim kašnjenjem  $[y(t), y(t - \tau), y(t - 2\tau), \dots, y(t - 2n\tau)]$  izvedena iz samo jednog generičkog signala.



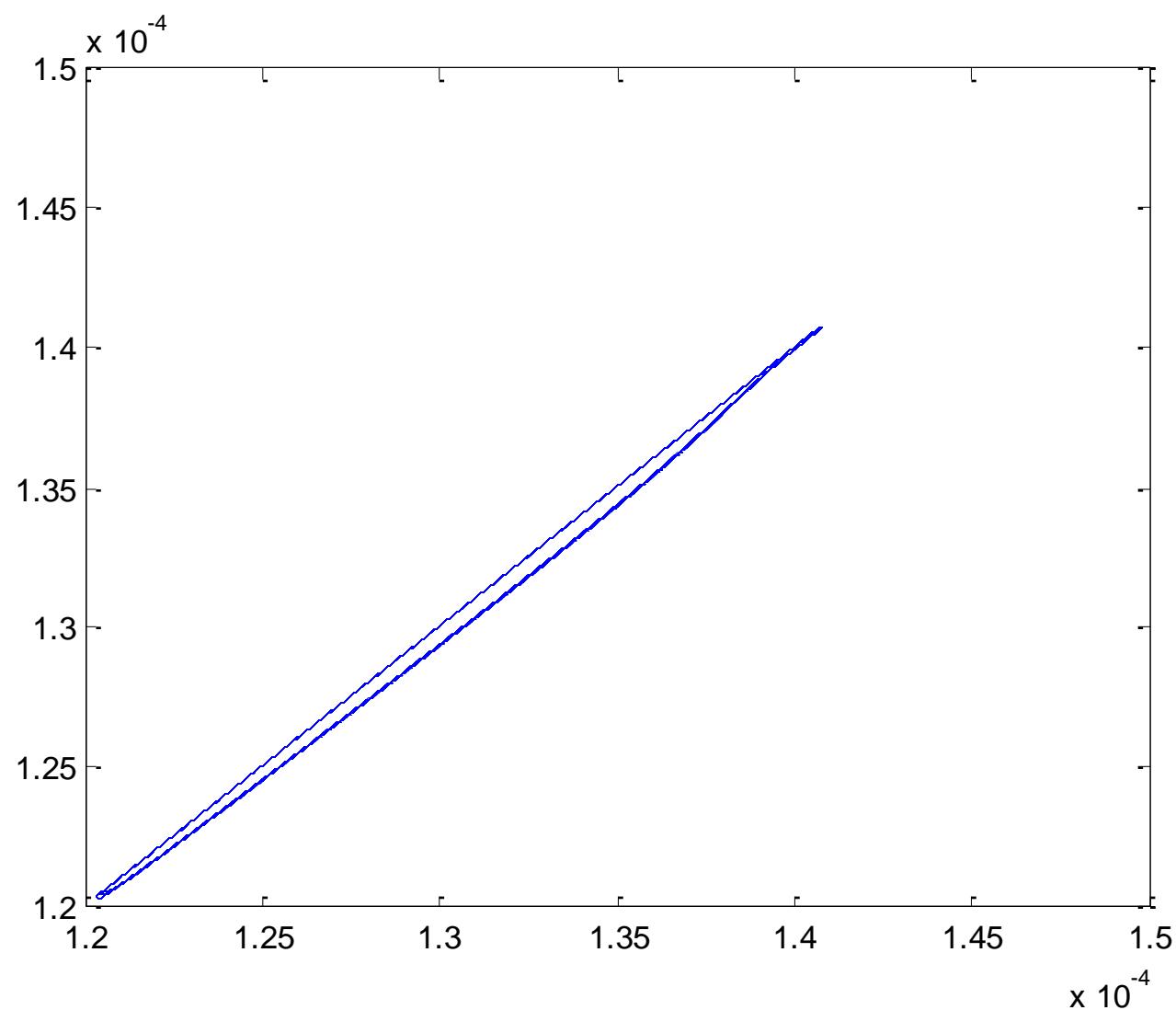
F. Takens (1981). "Detecting strange attractors in turbulence". In D. A. Rand and L.-S. Young. Dynamical Systems and Turbulence, Lecture Notes in Mathematics, vol. 898. Springer-Verlag. pp. 366–381.

## Polazna vremenska serija

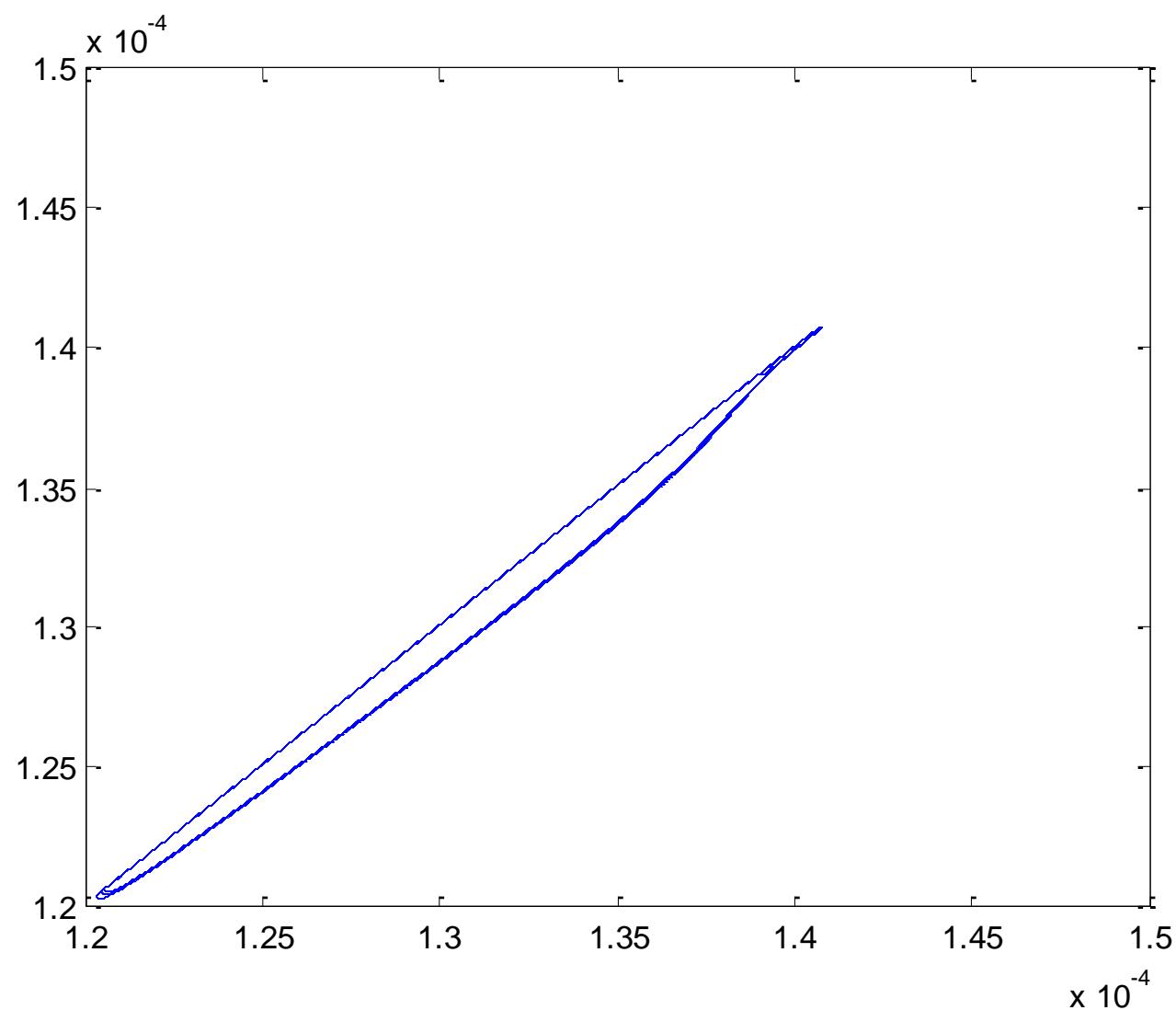




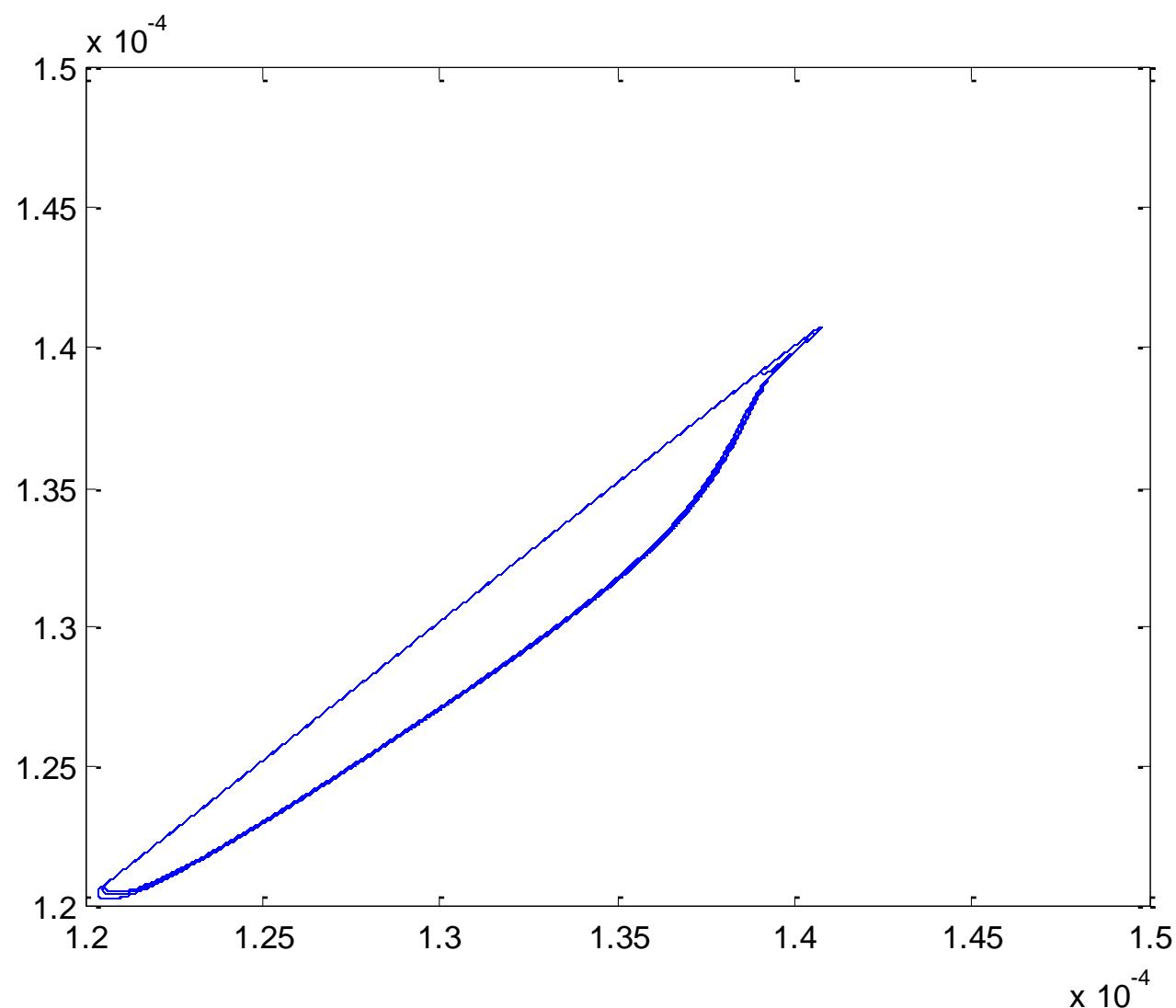
$$\tau = 1$$

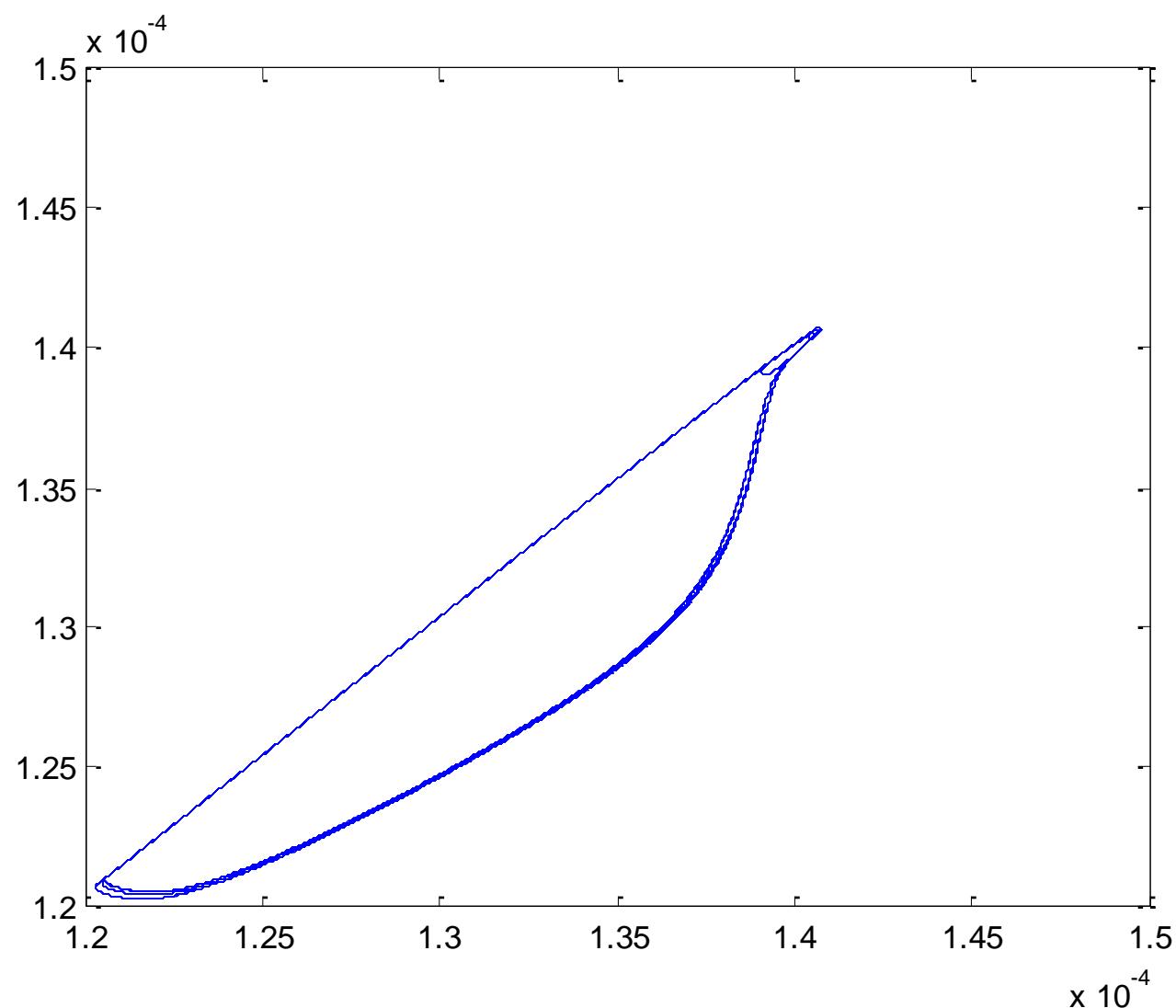


$\tau = 10$

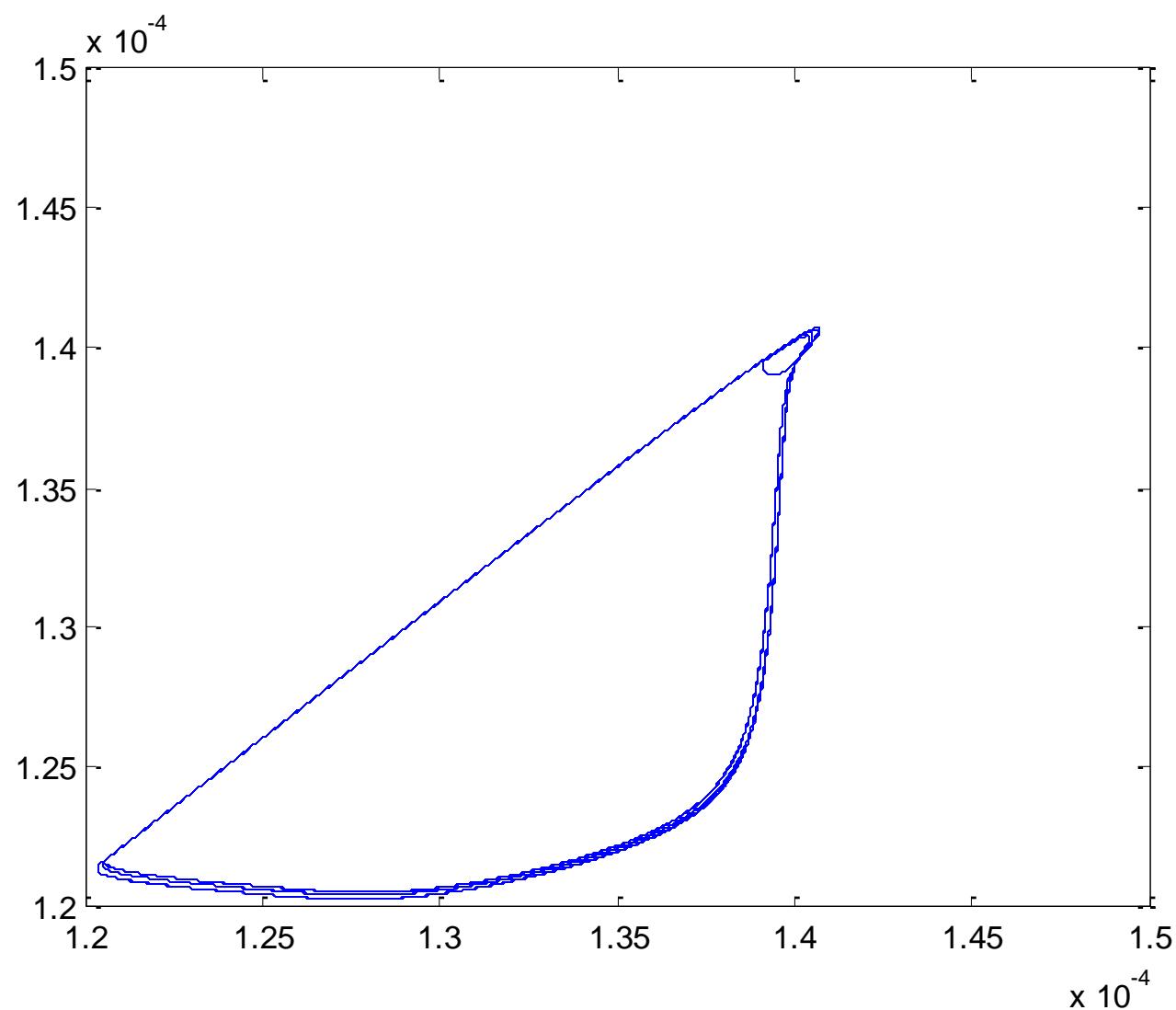


$\tau = 20$

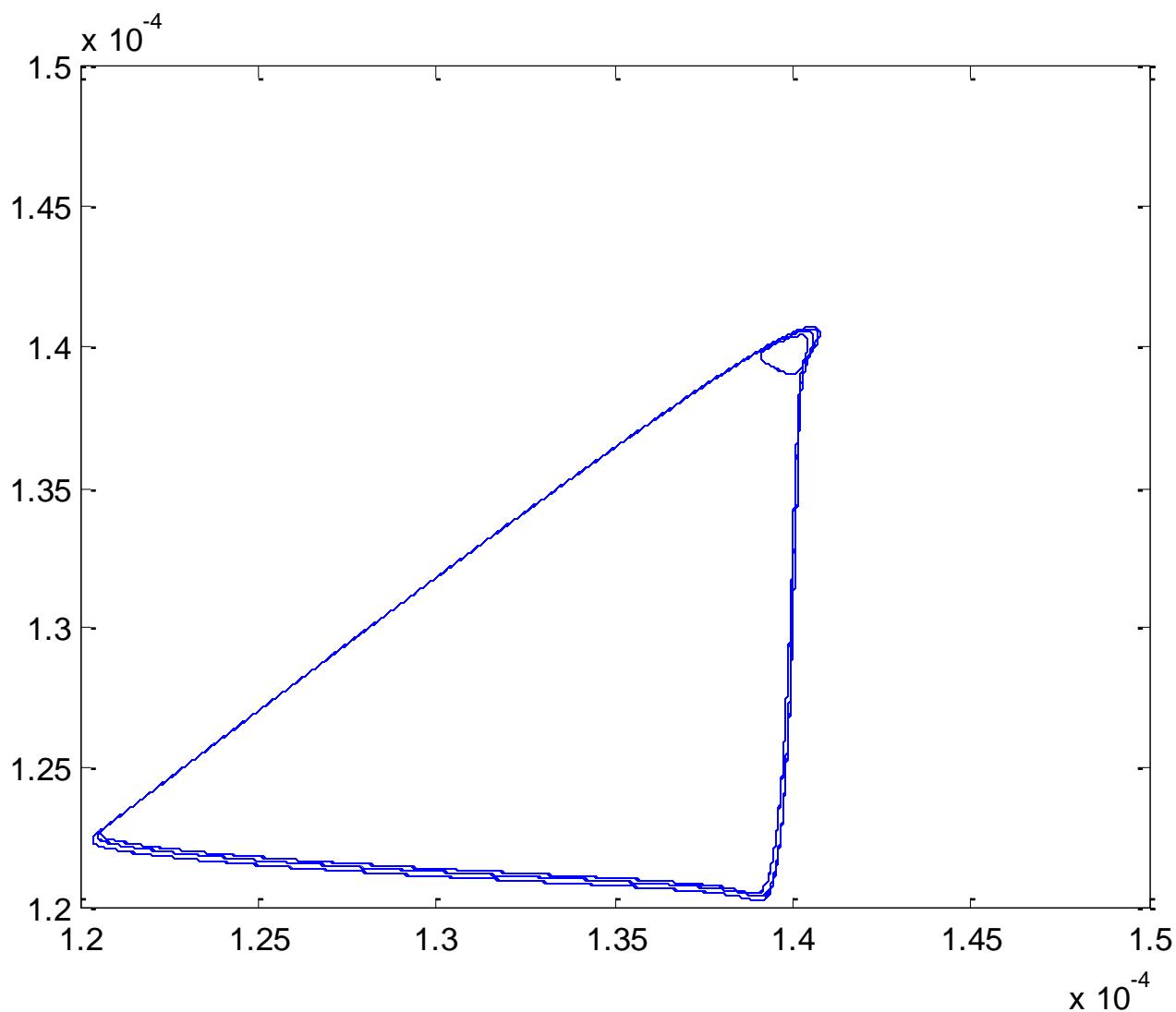




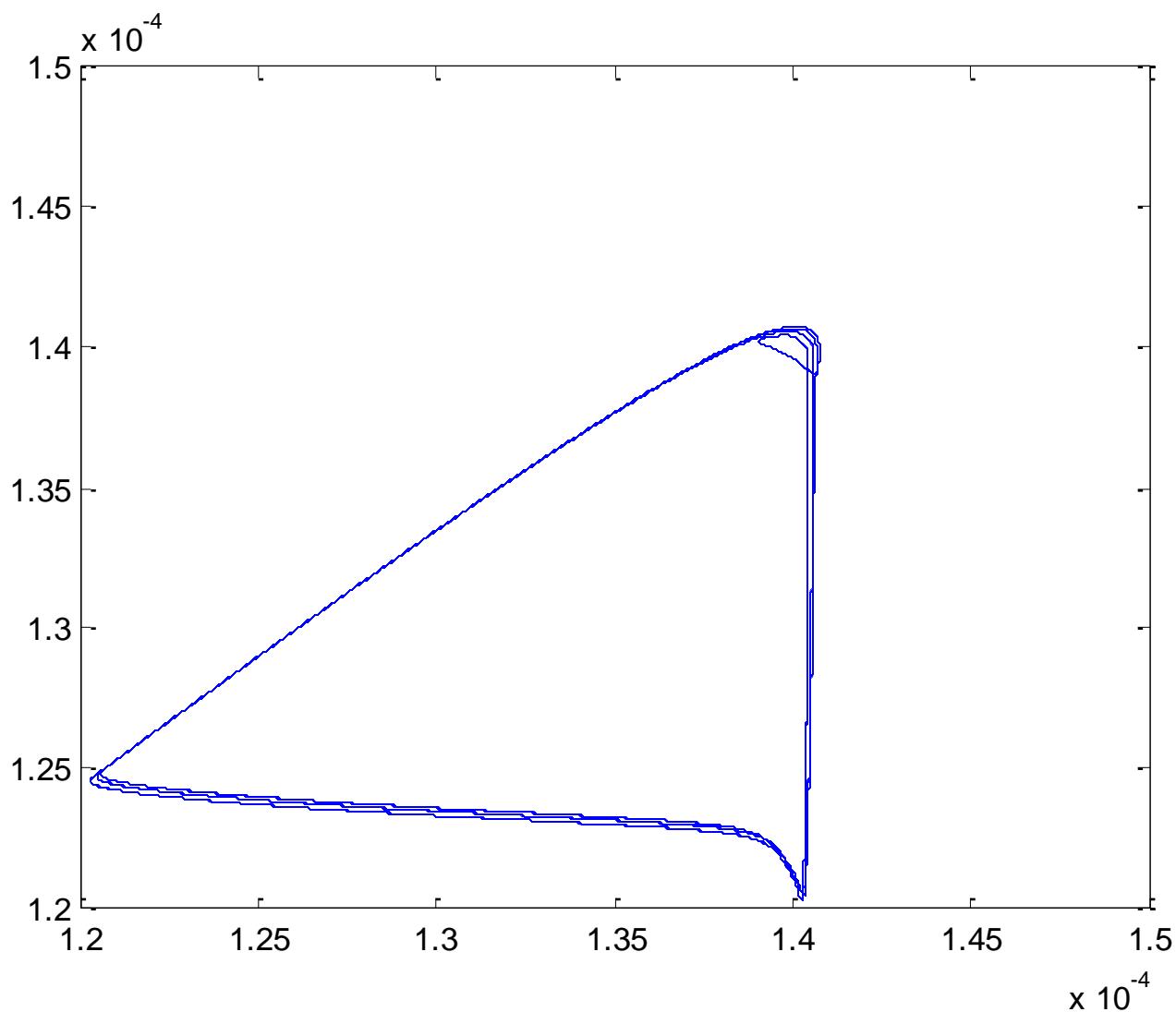
$\tau = 100$



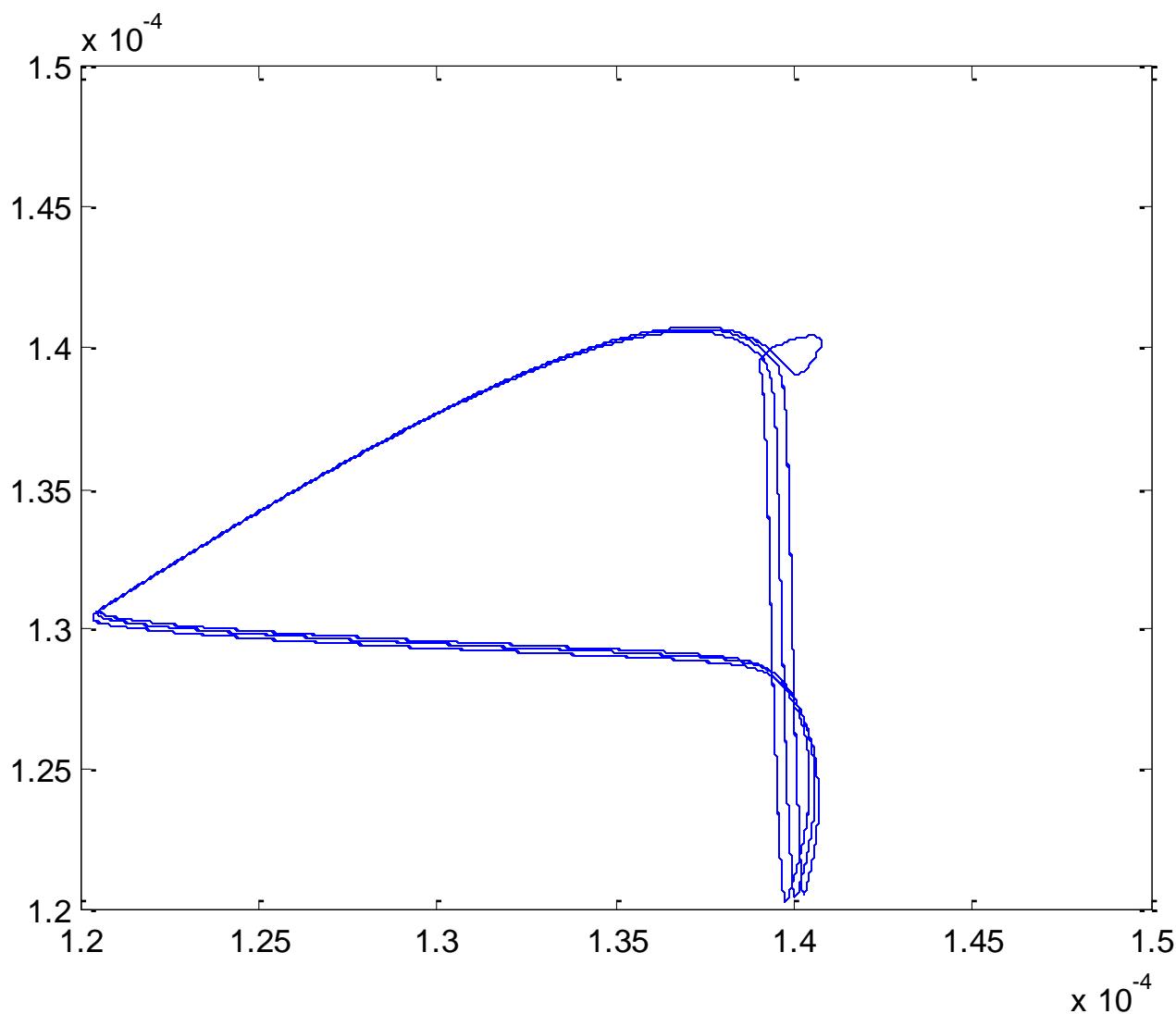
$\tau = 250$



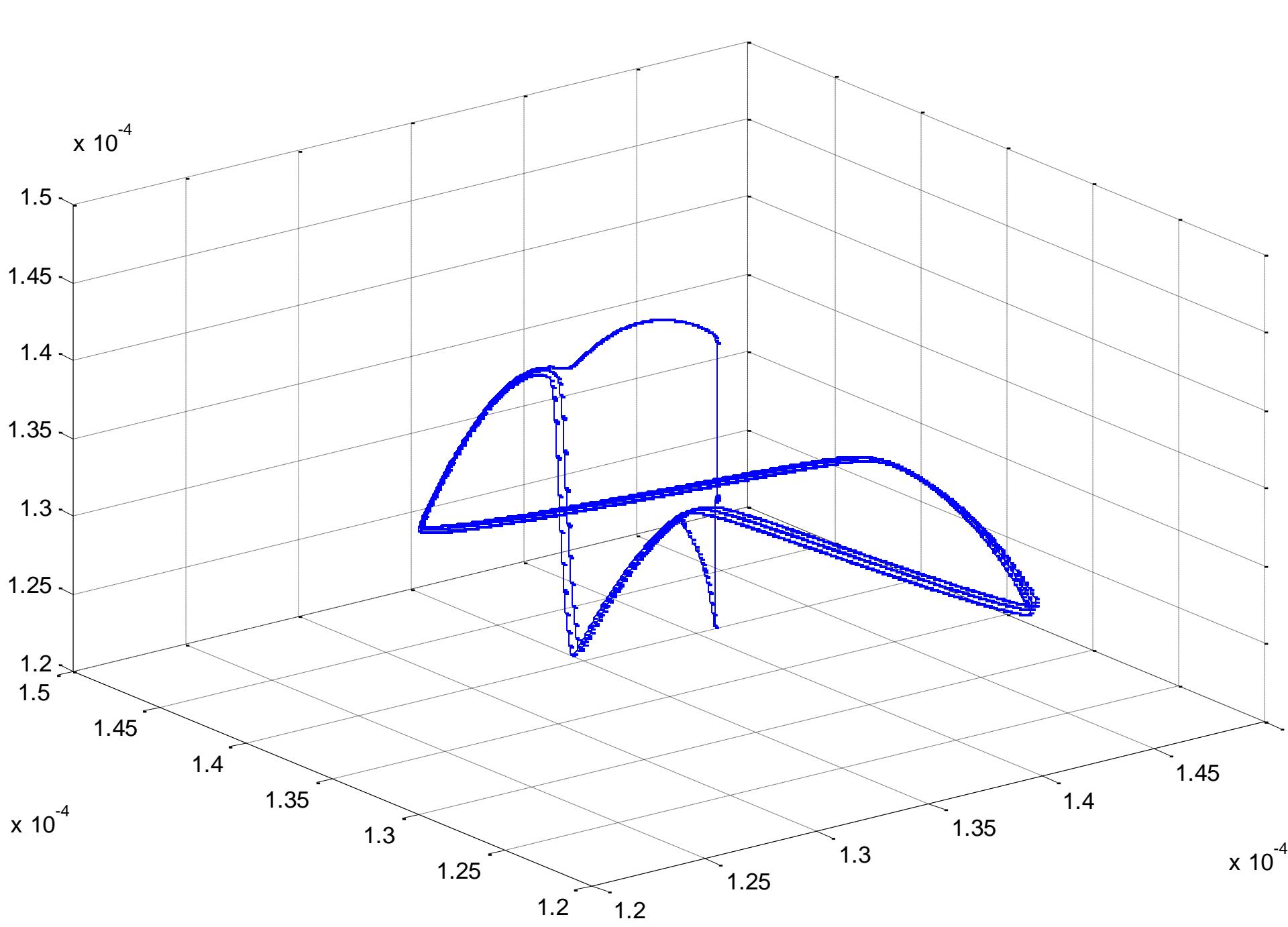
$\tau = 500$



$\tau = 1000$

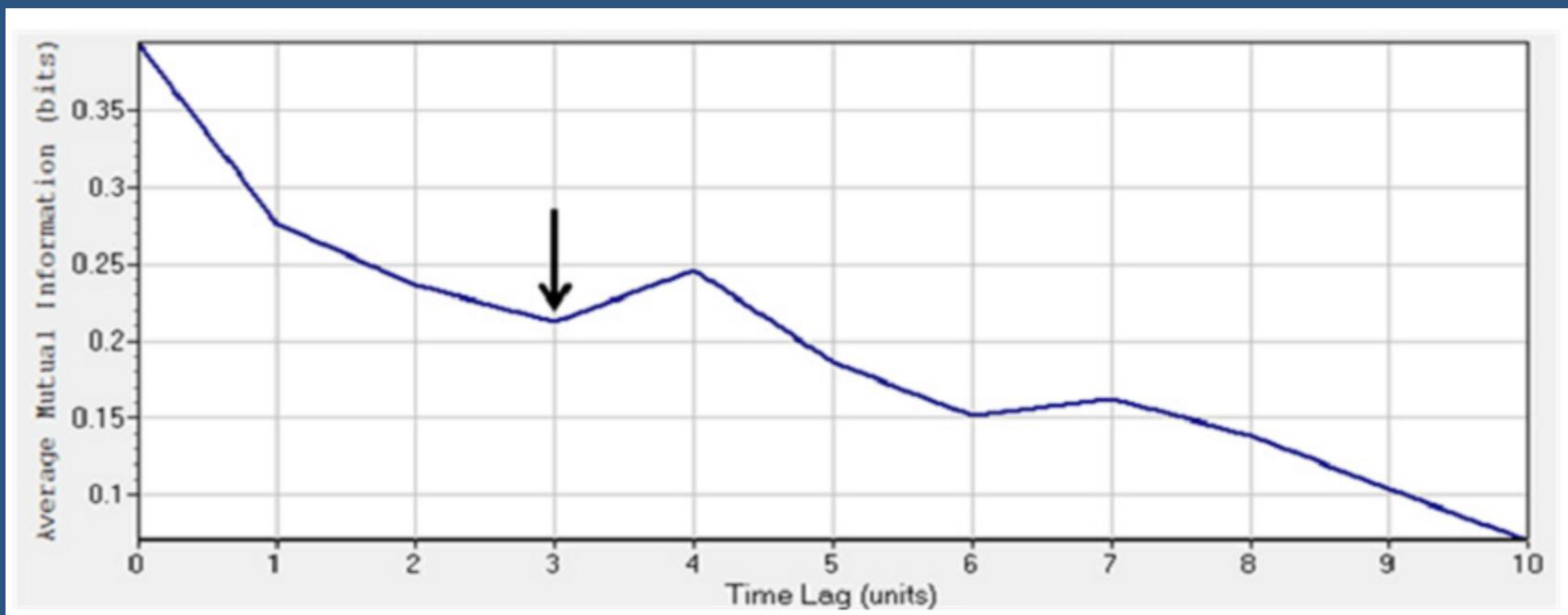


$\tau = 2500$



Vreme kašnjenja  $\tau$  se bira kao prvi minimum funkcije uzajamne informacije ‘mutual information function’ - probabilističke mere stepena u kome je  $x(t+\tau)$  korelisan sa  $x(t)$  za datu vrednost  $\tau$ .

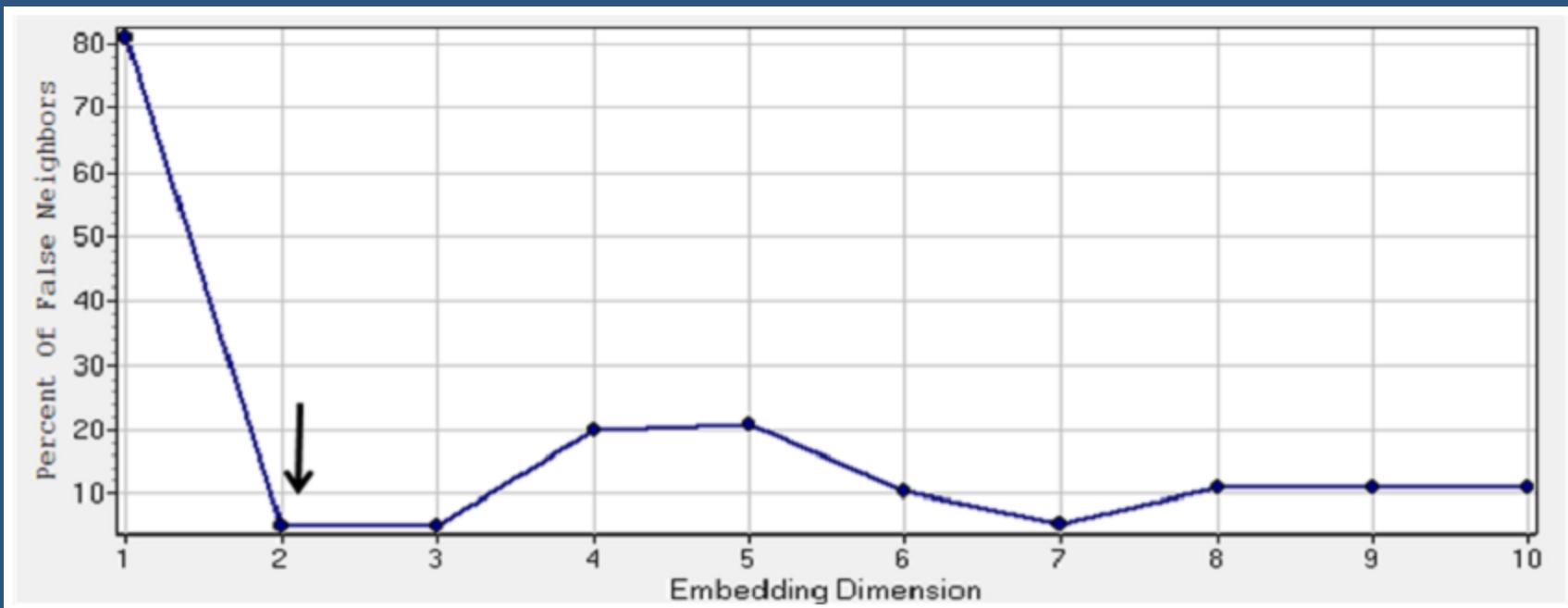
$$I(X; Y) = \sum_{y \in Y} \sum_{x \in X} p(x, y) \log \left( \frac{p(x, y)}{p(x) p(y)} \right),$$



**Dimenzija atraktora m se bira tehnikom lažnih najbližih suseda 'false nearest neighbors'.**

**Ovaj metod određuje procenat bliskih tačaka na rekonstruisanom atraktoru, koje ostaju bliske i kada se dimenzija atraktora poveća za 1.**

**Za vrednost parametra m koja odgovara dimenziji atraktora procenat lažnih suseda pada na nulu.**



# Razlaganje po singularnim vrednostima –

postupak sličan razlaganju na svojstvene vrednosti, ali primenljiv i na nekvadratne (pravougaone) matrice.

## *Singular value decomposition (SVD)*

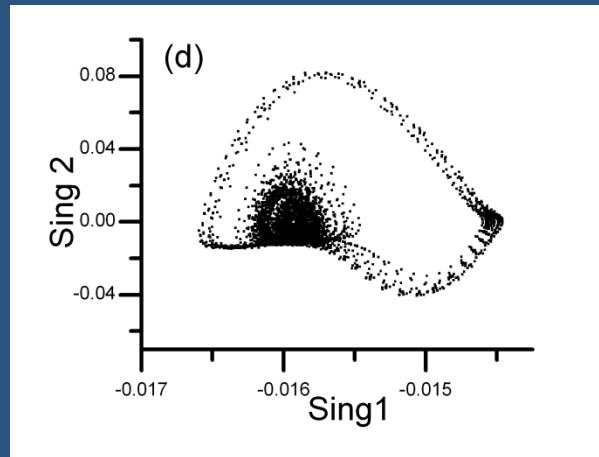
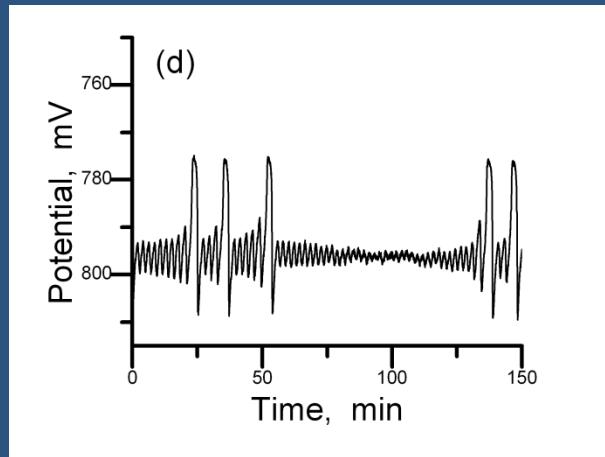
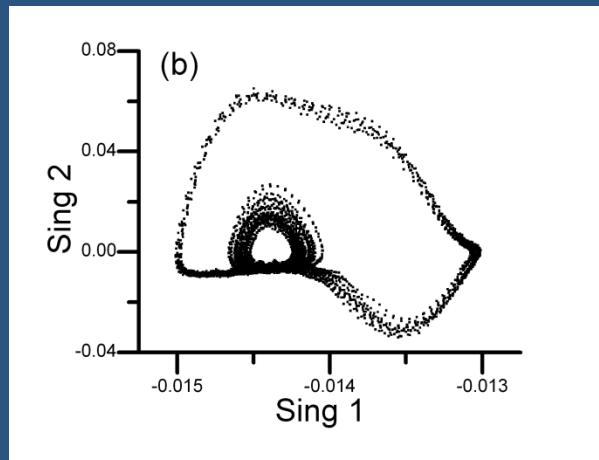
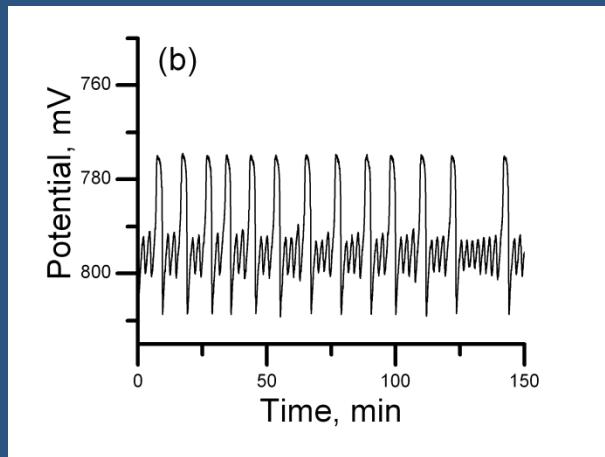
Matrica trajektorije

$$A = \begin{bmatrix} Y_1 \\ Y_2 \\ \vdots \\ Y_N \end{bmatrix} = \begin{bmatrix} \nu(\tau) & \nu(2\tau) & \dots & \nu(d\tau) \\ \nu(2\tau) & \nu(3\tau) & \dots & \nu((d+a)\tau) \\ \vdots & \vdots & \ddots & \vdots \\ \nu(N\tau) & \nu((N+1)\tau) & \dots & \nu((N+1-d)\tau) \end{bmatrix}$$

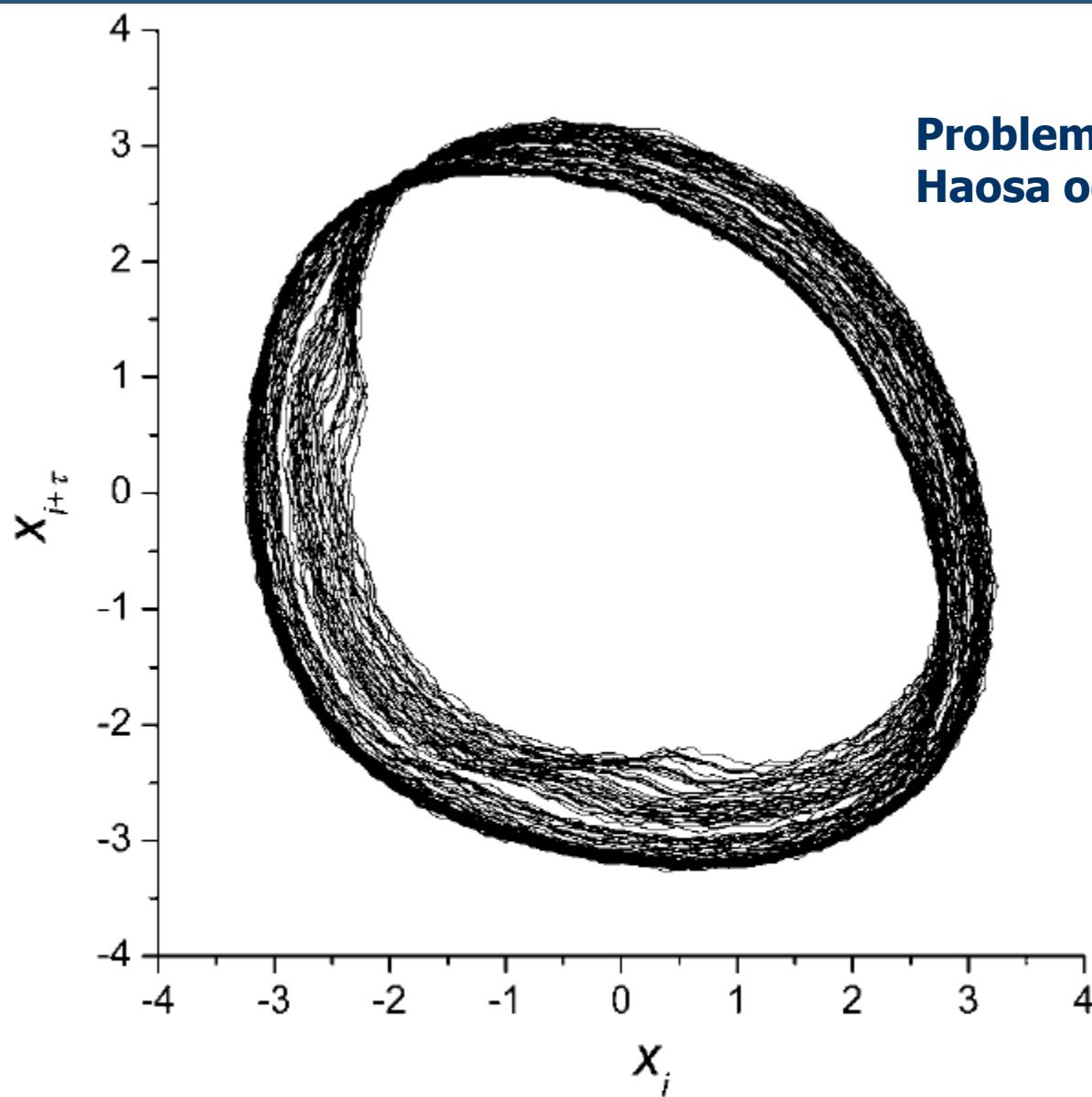
$$\begin{bmatrix} A_{11} & \dots & A_{N1} \\ \vdots & \ddots & \vdots \\ \vdots & \dots & \vdots \\ \vdots & \dots & \vdots \\ A_{1d} & \dots & A_{Nd} \end{bmatrix}_{N \times d} = \begin{bmatrix} V_{11} & \dots & V_{N1} \\ \vdots & \ddots & \vdots \\ \vdots & \dots & \vdots \\ \vdots & \dots & \vdots \\ V_{1d} & \dots & V_{Nd} \end{bmatrix}_{N \times d} X \begin{bmatrix} S_1 & 0 & 0 \\ \vdots & \ddots & \vdots \\ 0 & 0 & S_d \end{bmatrix}_{d \times d} X^T \begin{bmatrix} U_{11} & \dots & U_{1d} \\ \vdots & \ddots & \vdots \\ U_{d1} & \dots & U_{dd} \end{bmatrix}_{d \times d}$$

Postupak SVD obezbeđuje dobijanje singularnih vrednosti u formi opadajućeg intenziteta. U idealnom slučaju samo nekoliko singularnih vektora odgovara singularnim vrednostima koje daju značajan doprinos, dok ostalima odgovaraju nule. Postupak se koristi i za eliminaciju šuma iz signala. Razvijen je i postupak kvantifikacije haosa određivanjem tzv. Ljapunovljevih eksponenata primenom SVD tehnike.

# Primeri rekonstruisanih atraktora eksperimentalno snimljenih signala elektrodnog potencijala u oscilatornoj reakciji BL

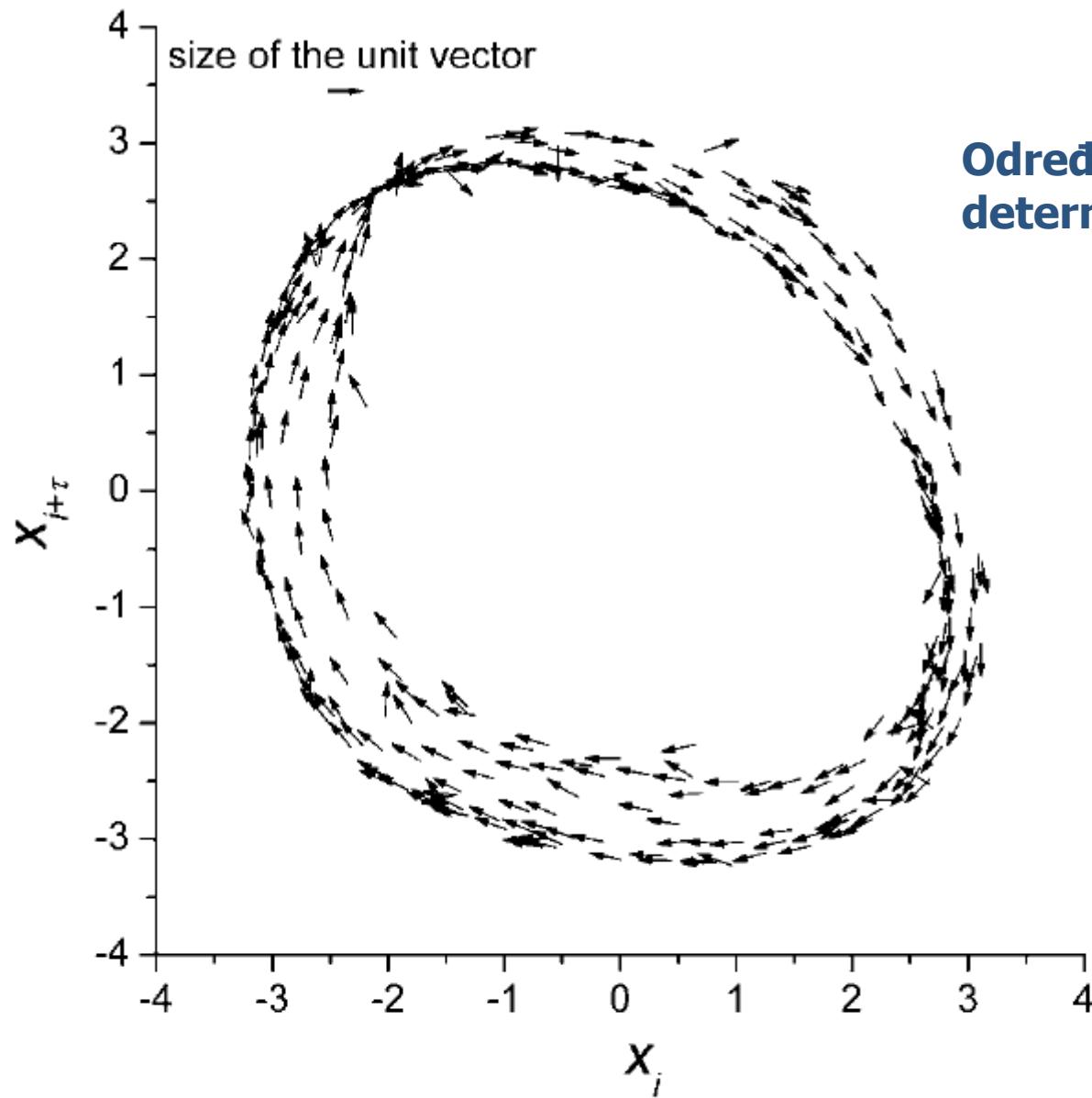


A. Z. Ivanović, Ž. D. Čupić, M. M. Janković Lj. Z. Kolar-Anić and S. R. Anić, The chaotic sequences in the Bray–Liebhafsky reaction in an open Reactor, *Phys. Chem. Chem. Phys.*, 2008, 10, 5848–5858



**Problem razlikovanja  
Haosa od eksp. šuma**

**Figure 5.** Reconstructed phase space obtained with the optimal embedding parameters:  $\tau = 65$  and  $m = 5$ .



## Određivanje faktora determinizma

**Figure 6.** Determinism test. The approximated vector field for the embedding space reconstructed with  $\tau = 65$  and  $m = 5$ . The pertaining determinism factor is  $\kappa = 0.83$ .

**Računa se usrednjeni vektor polja brzina za svaki delić prostora k, kroz koji prolazi trajektorija.  
Zatim se intenziteti ovih vektora usrednje po celom atraktoru**

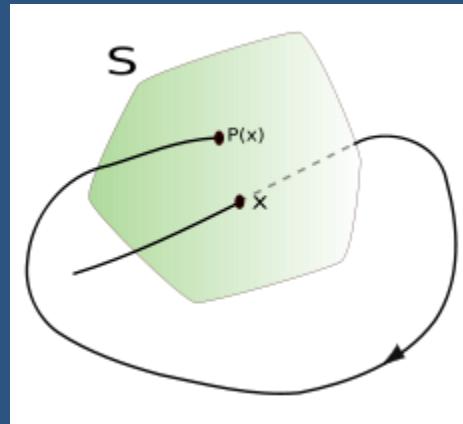
$$\mathbf{V}_k = \frac{1}{P_k} \sum_{i=1}^{P_k} \mathbf{e}_i,$$

**Ukoliko je rezultat blizak jedinici sistem je deterministički  
Ako je rezultat niži od jedinice, sistem pokazuje  
stohastičku komponentu dinamike**

# Sadržaj II časa

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  - Cobweb dijagrami
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# Poenkareovi preseci



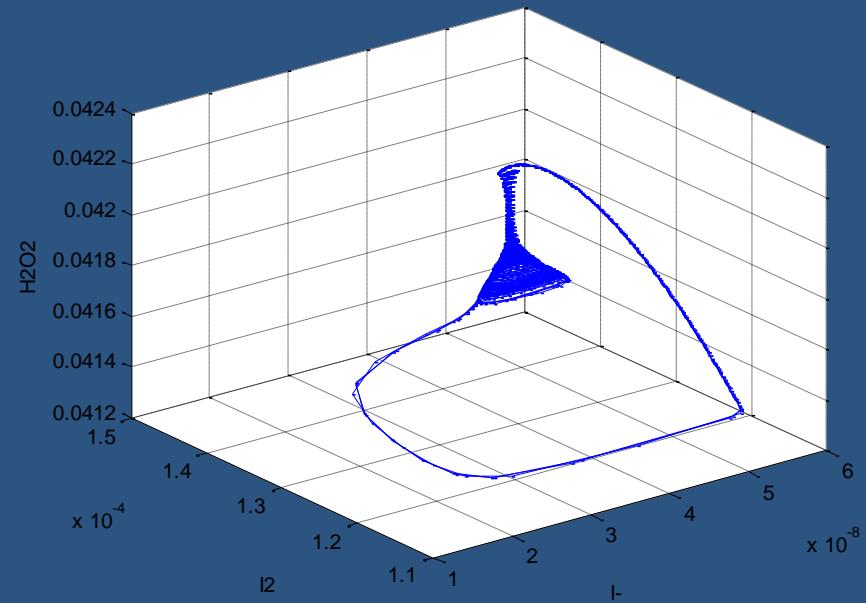
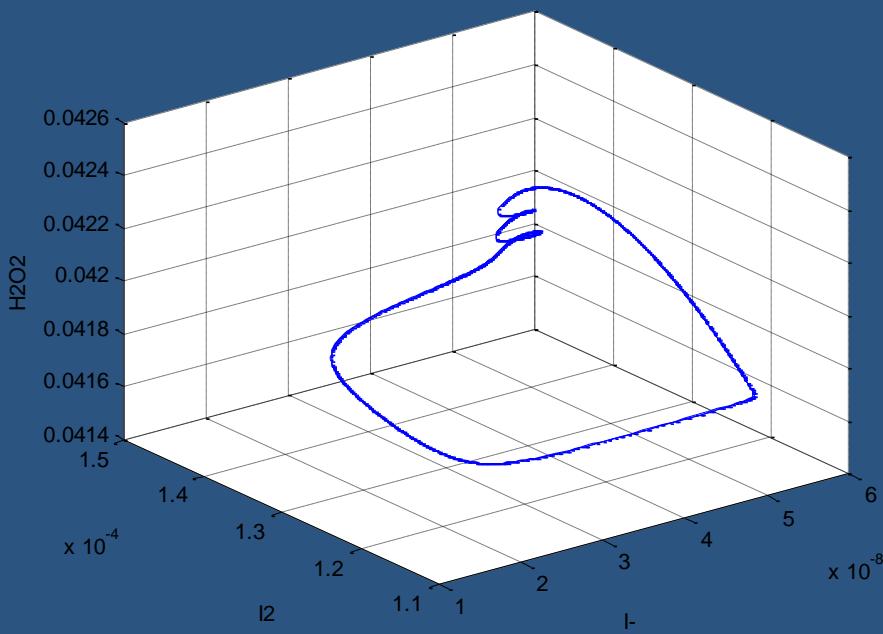
Dimenzionalnost dinamičkog sistema se smanjuje i  
Kontinualni dinamički sistem se diskretizuje

**S. N. Blagojević, Ž. Čupić, A. Ivanović-Šašić and Lj. Kolar-Anić, " Mixed-mode Oscillations and Chaos in Return Maps of an Oscillatory Chemical Reaction " Russ. J. Phys. Chem. A, 13 (2015) 2349-2358.**

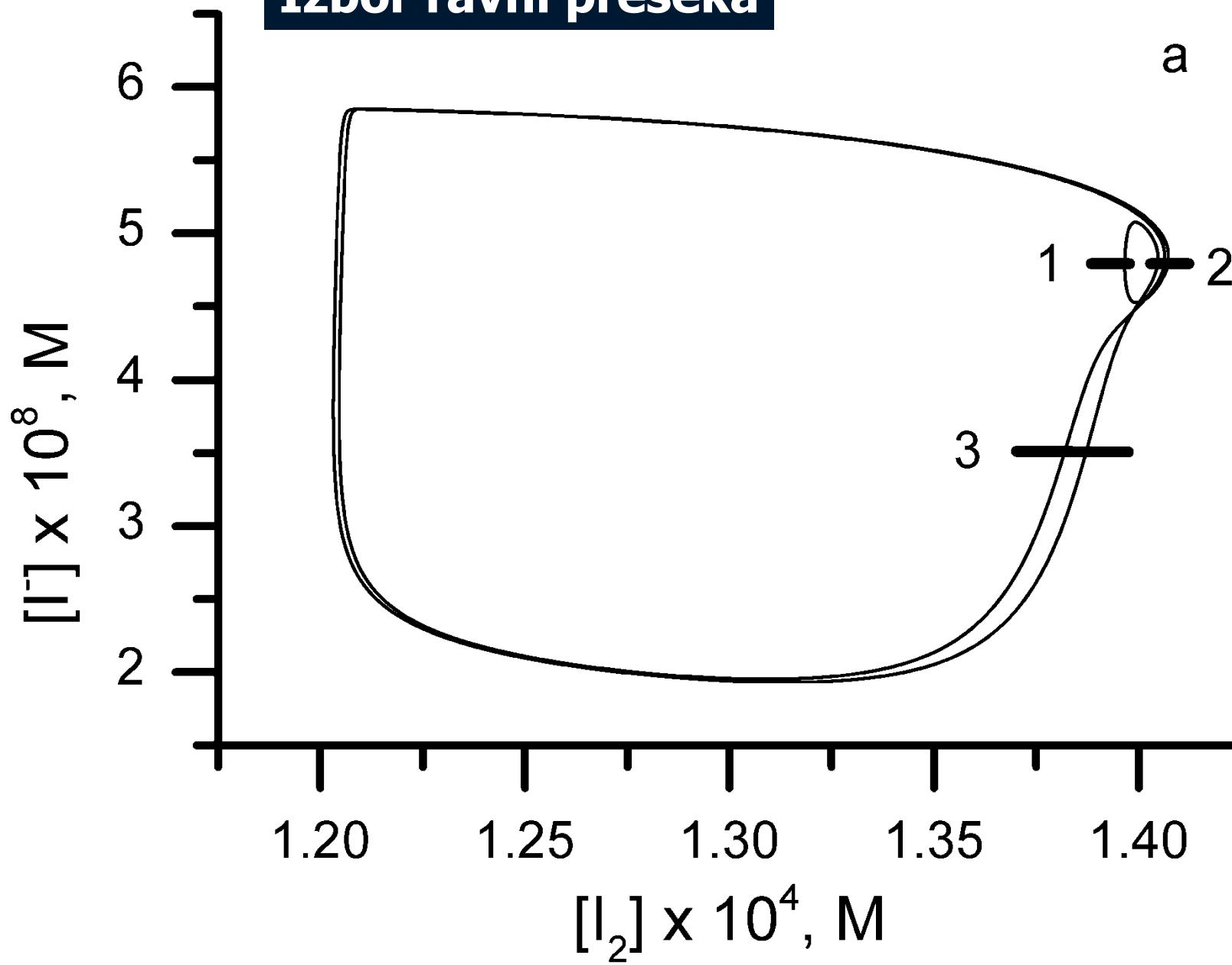
**Željko Čupić, Ana Ivanović-Šašić, Stevan Blagojević, Slavica Blagojević, Ljiljana Kolar-Anić, Slobodan Anić, " Return maps analysis of the highly nonlinear Bray-Liebhafsky reaction model " Reaction Kinetics, Mechanisms and Catalysis, 118 (2016) 27-38.**

Periodični sistemi imaju diskretan mali broj tačaka u Poenkareovom preseku

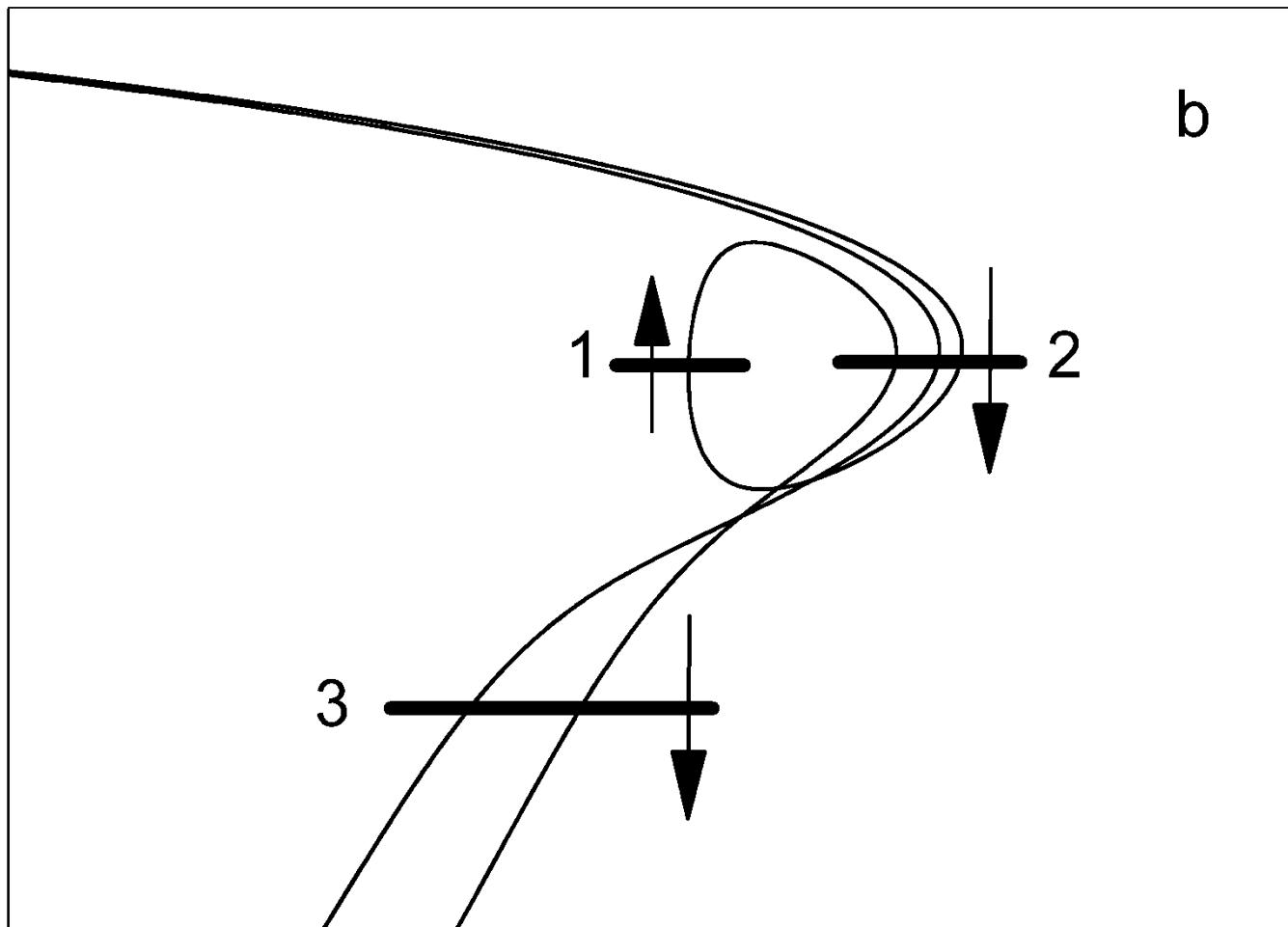
Haotični sistemi imaju “neograničen broj” tačaka u Poenkareovom preseku



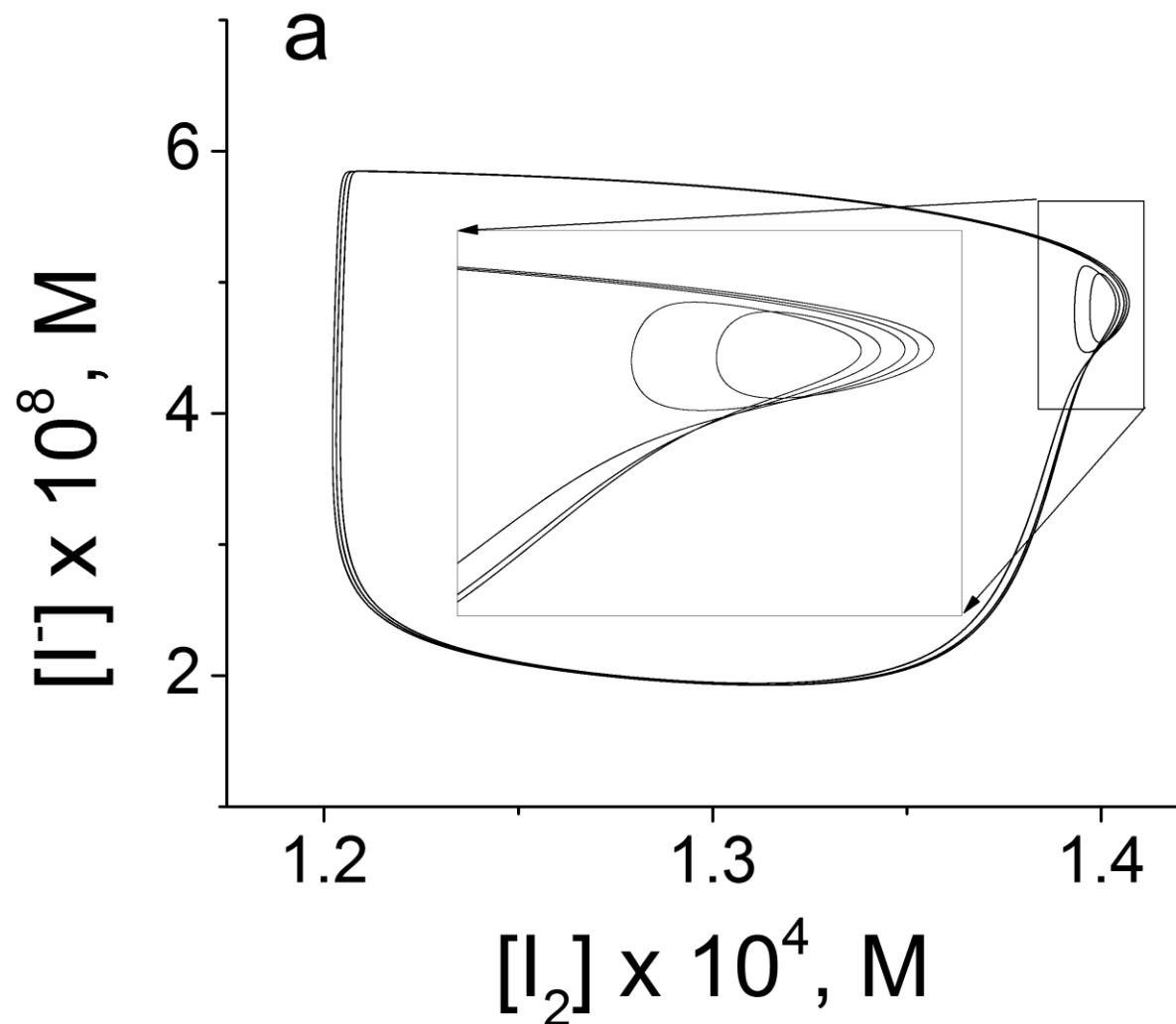
## Izbor ravni preseka



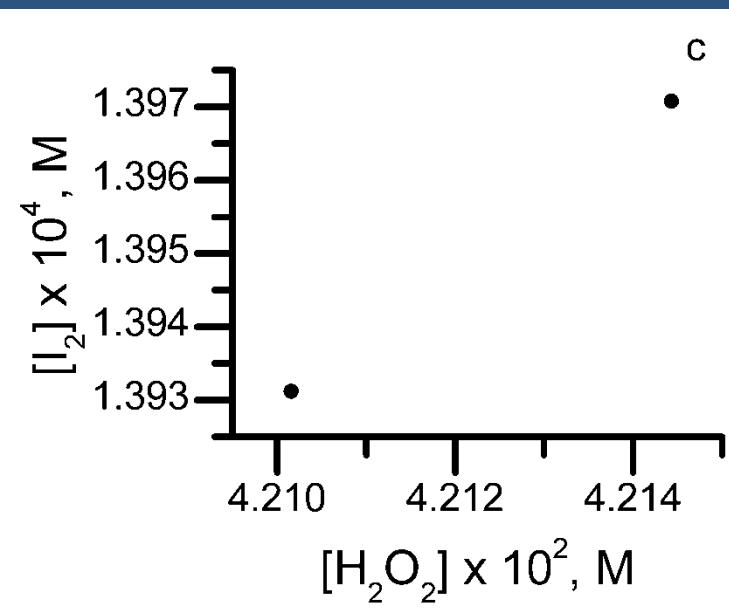
b



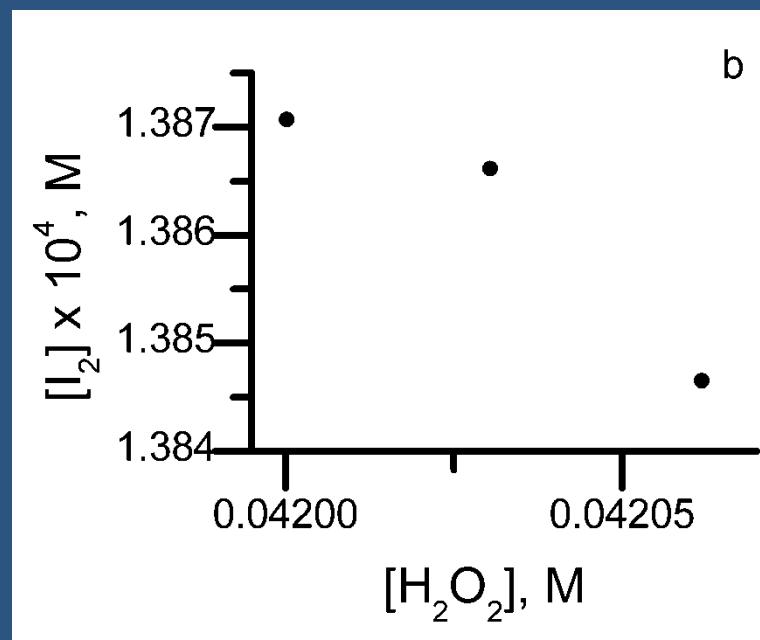
$$j_0 = 4.8550 \times 10^{-3} \text{ min}^{-1} \quad (2^1 1^1)$$



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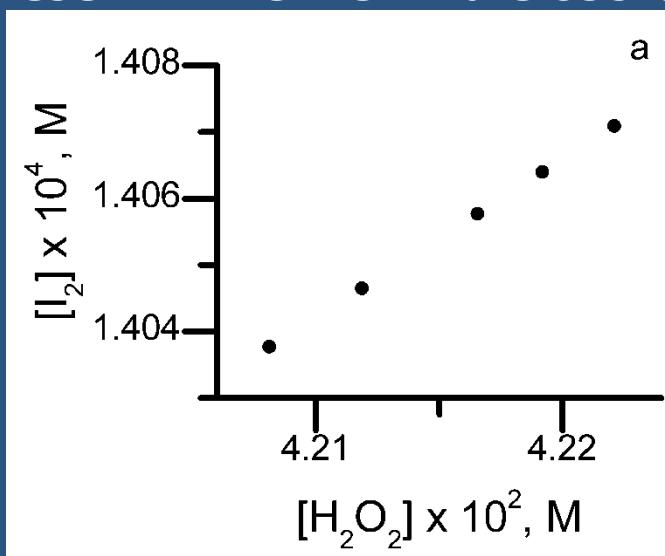


Presek 1 – samo male oscilacije



Presek 3 – samo velike oscilacije

Presek 2 – velike i male oscilacije

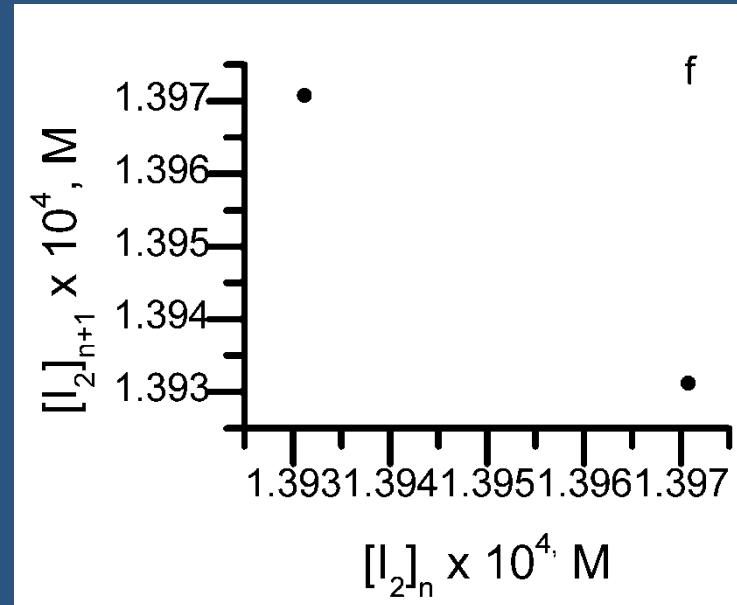
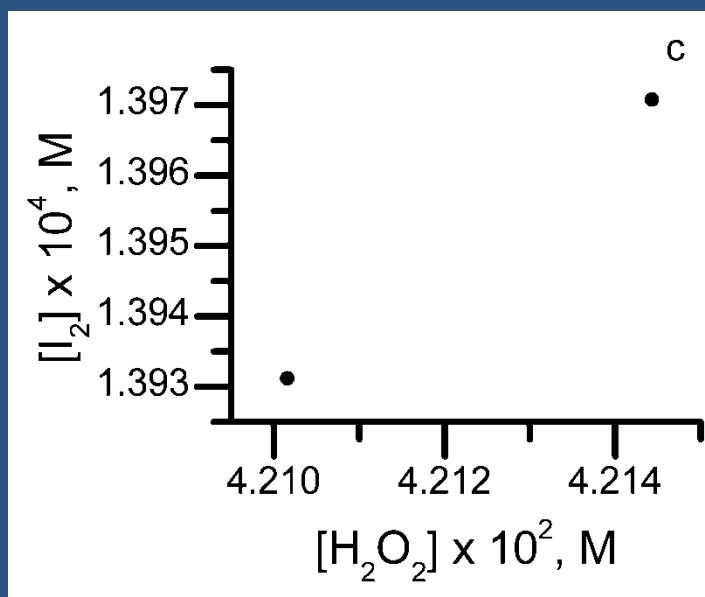


# Iteracione mape – povratne mape

Iteracione mape nam daju mogućnost da prikažemo Poenkareov presek u formi diskretizovanog dinamičkog sistema.

$$j_0 = 4.8550 \times 10^{-3} \text{ min}^{-1} \quad (2^1 1^1)$$

**Presek 1 – samo male oscilacije**



Poenkareov presek



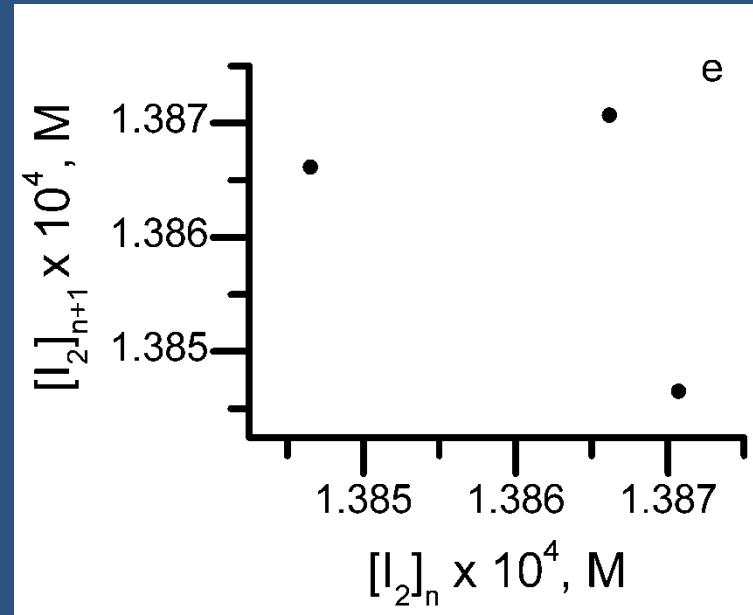
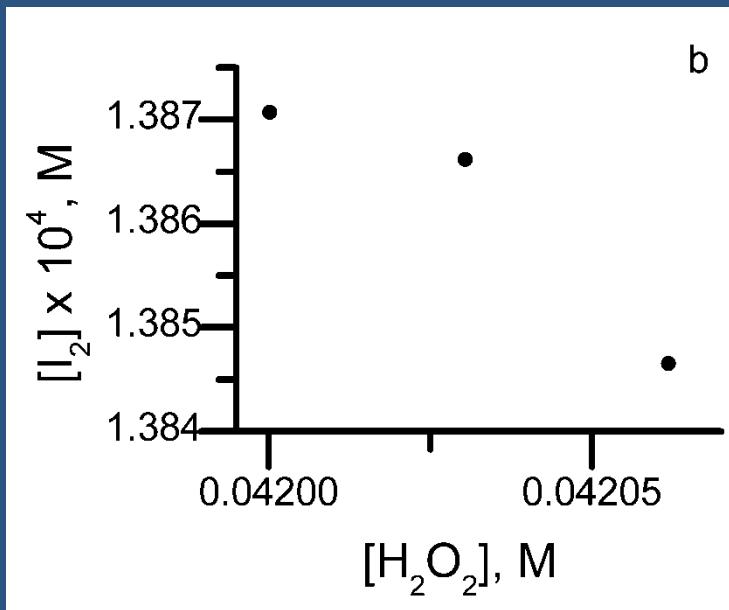
Poenkareova iteraciona mapa

# Iteracione mape – povratne mape

Iteracione mape nam daju mogućnost da prikažemo Poenkareov presek u formi diskretizovanog dinamičkog sistema.

$$j_0 = 4.8550 \times 10^{-3} \text{ min}^{-1} \quad (2^1 1^1)$$

**Presek 3 – samo velike oscilacije**



Poenkareov presek



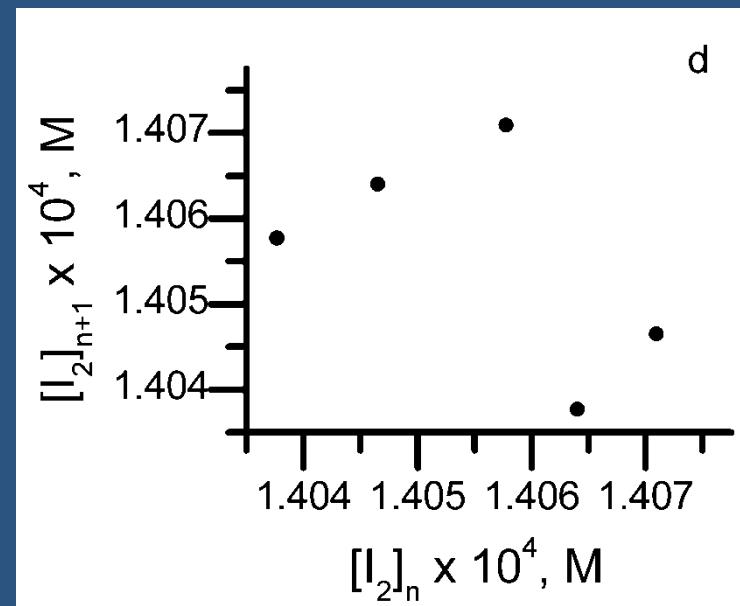
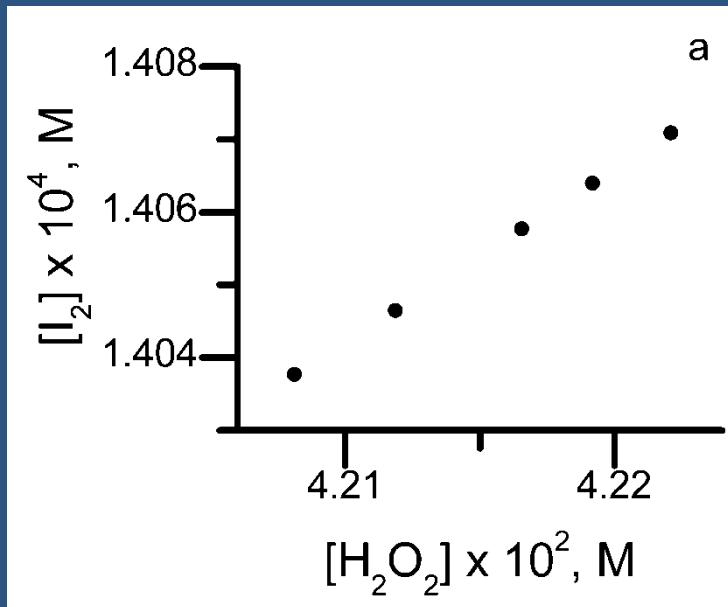
Poenkareova iteraciona mapa

# Iteracione mape – povratne mape

Iteracione mape nam daju mogućnost da prikažemo Poenkareov presek u formi diskretizovanog dinamičkog sistema.

$$j_0 = 4.8550 \times 10^{-3} \text{ min}^{-1} \quad (2^1 1^1)$$

**Presek 2 – male i velike oscilacije**



Poenkareov presek



Poenkareova iteraciona mapa

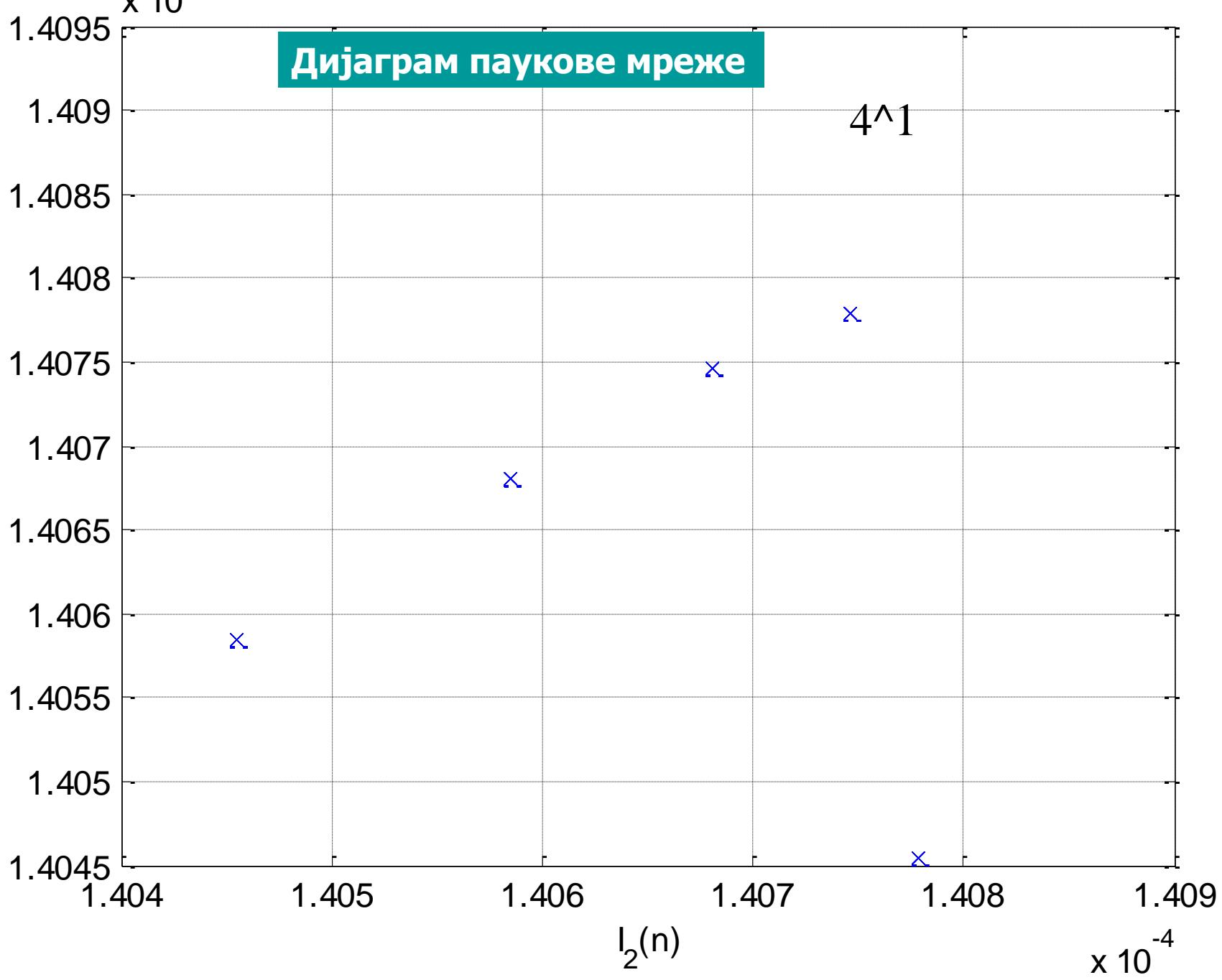
$I = 4.8 \times 10^{-8} M$  Velike i Male

$\times 10^{-4}$

## Дијаграм паукове мреже

$4^1$

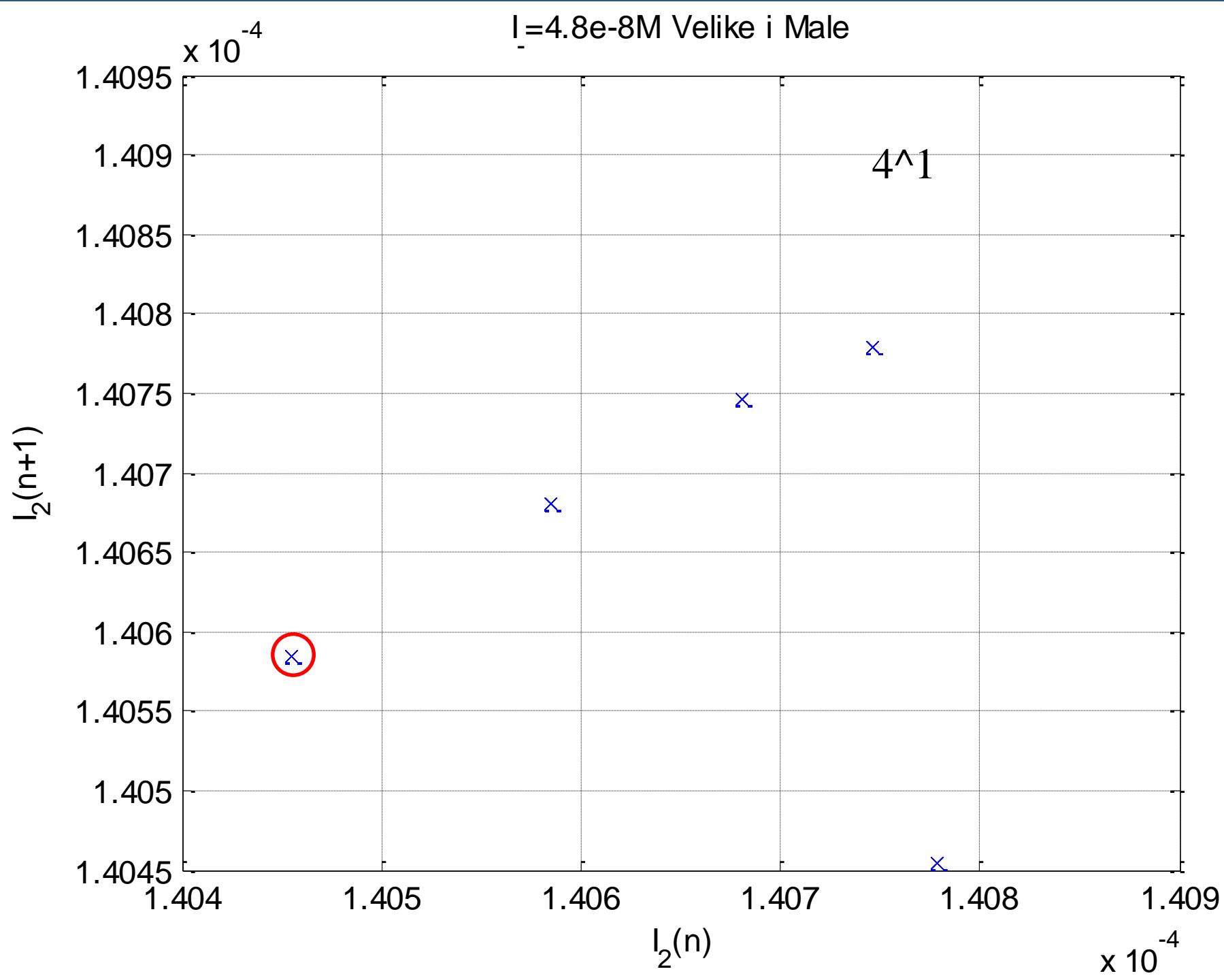
$I_2(n+1)$



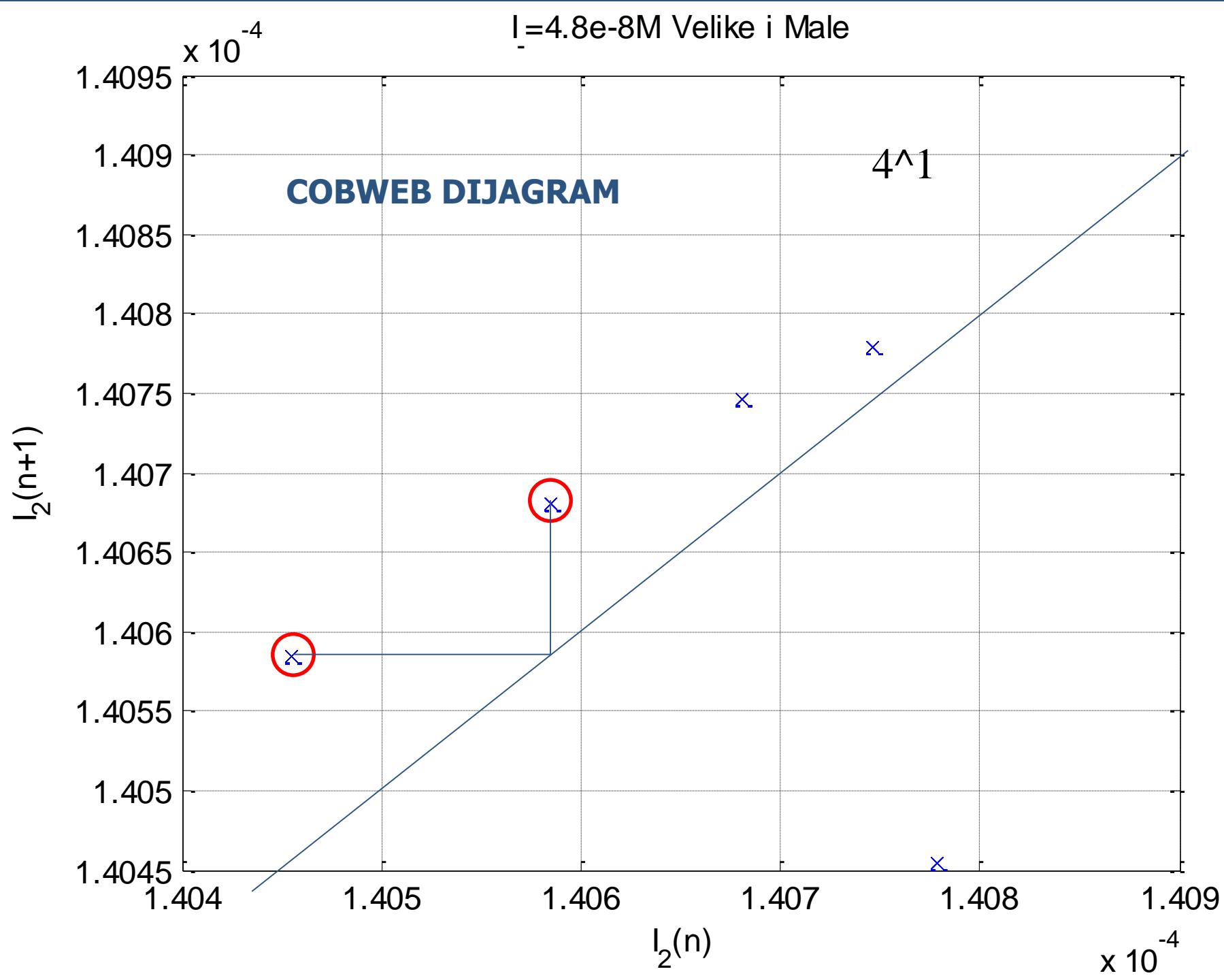
$I_2(n)$

$\times 10^{-4}$

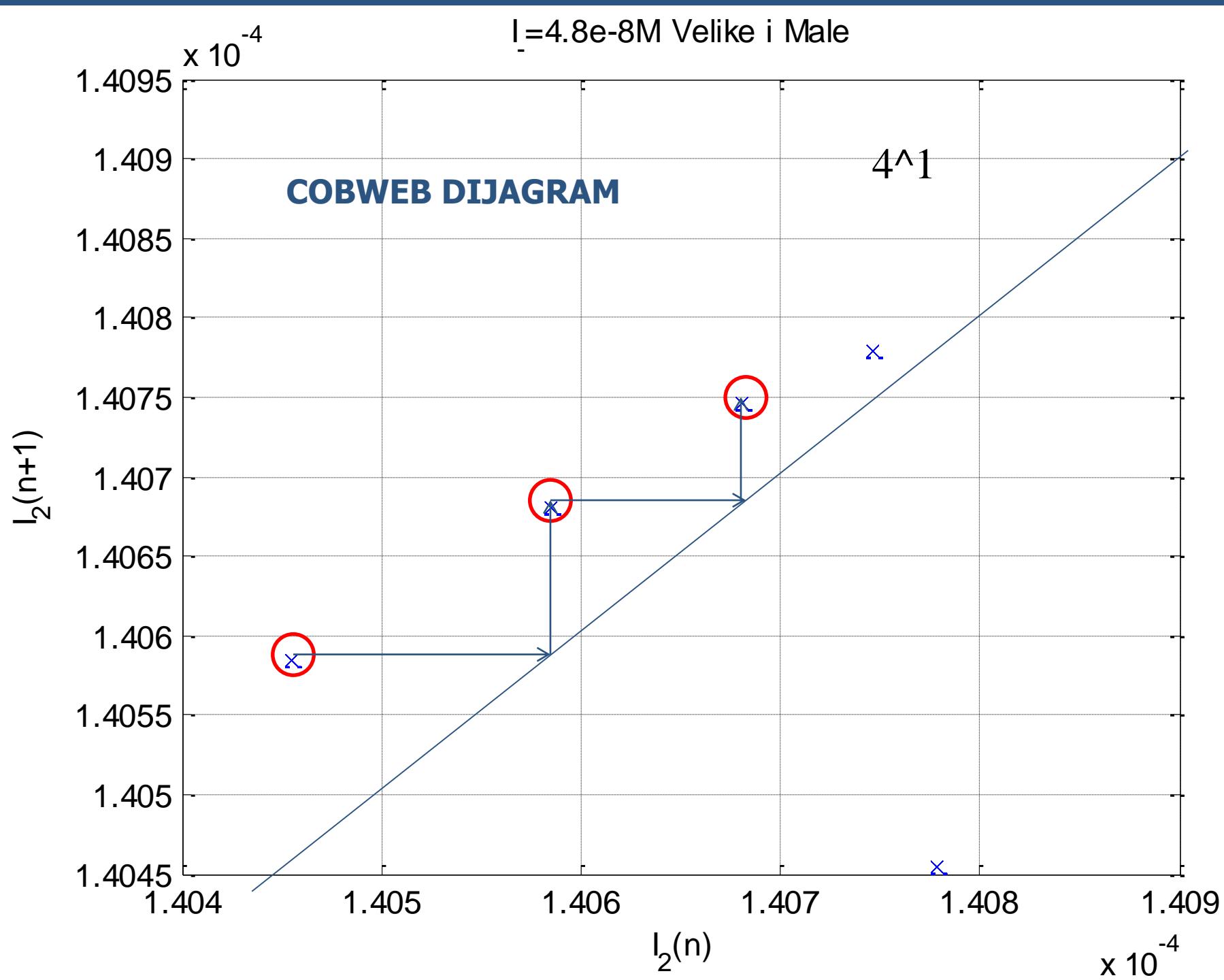
$I = 4.8 \times 10^{-8} M$  Velike i Male



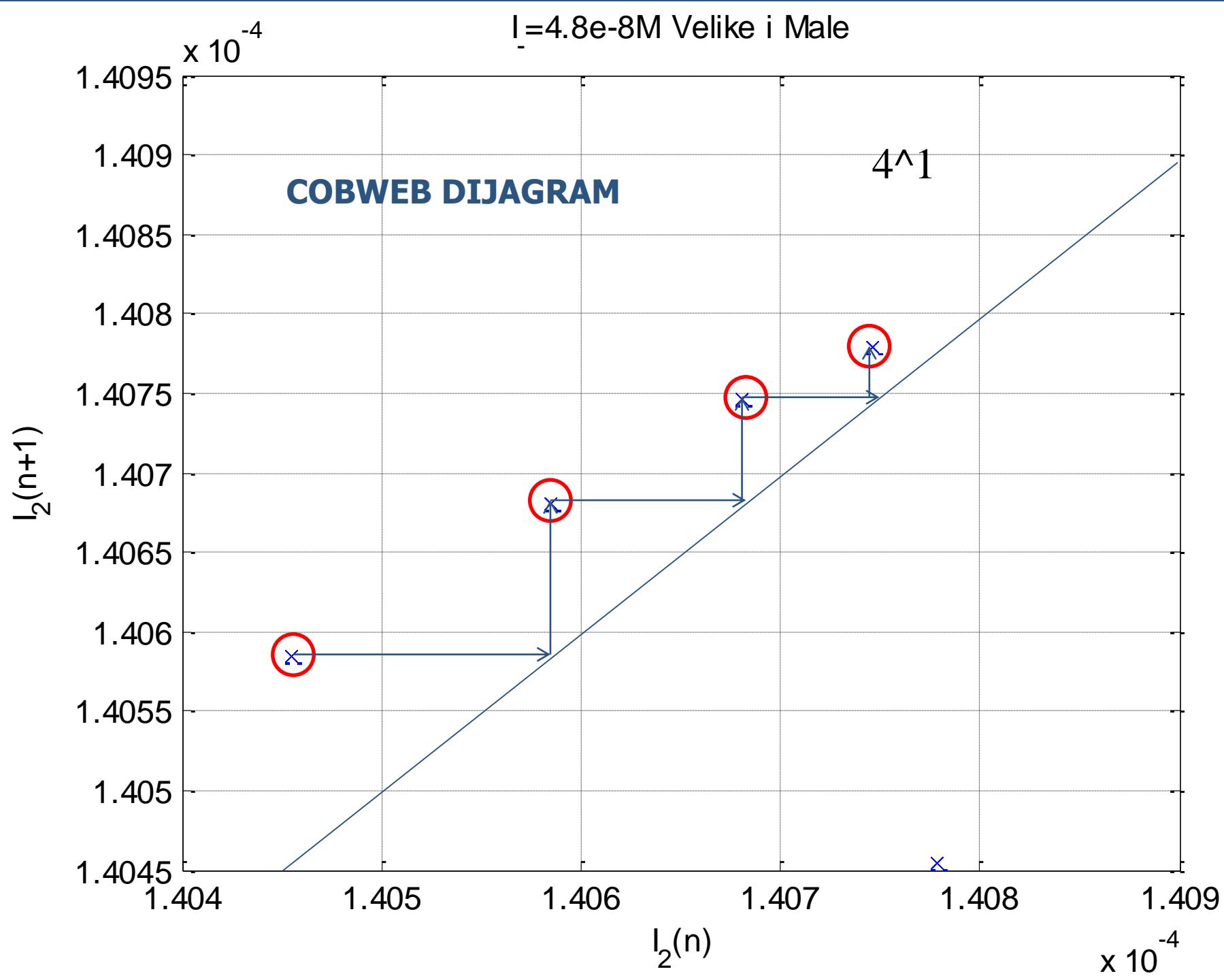
$I = 4.8 \times 10^{-8} M$  Velike i Male



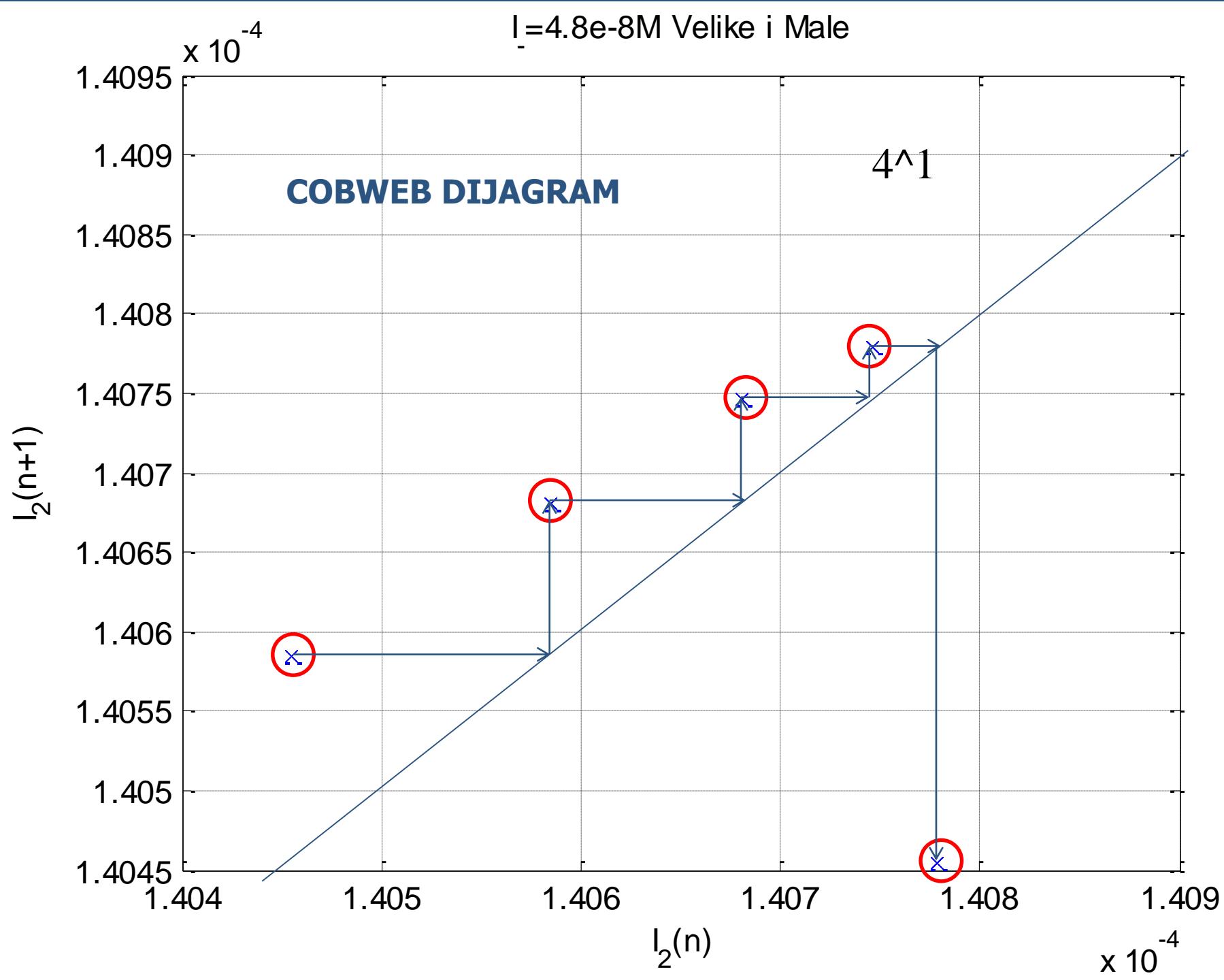
$I = 4.8 \times 10^{-8} M$  Velike i Male



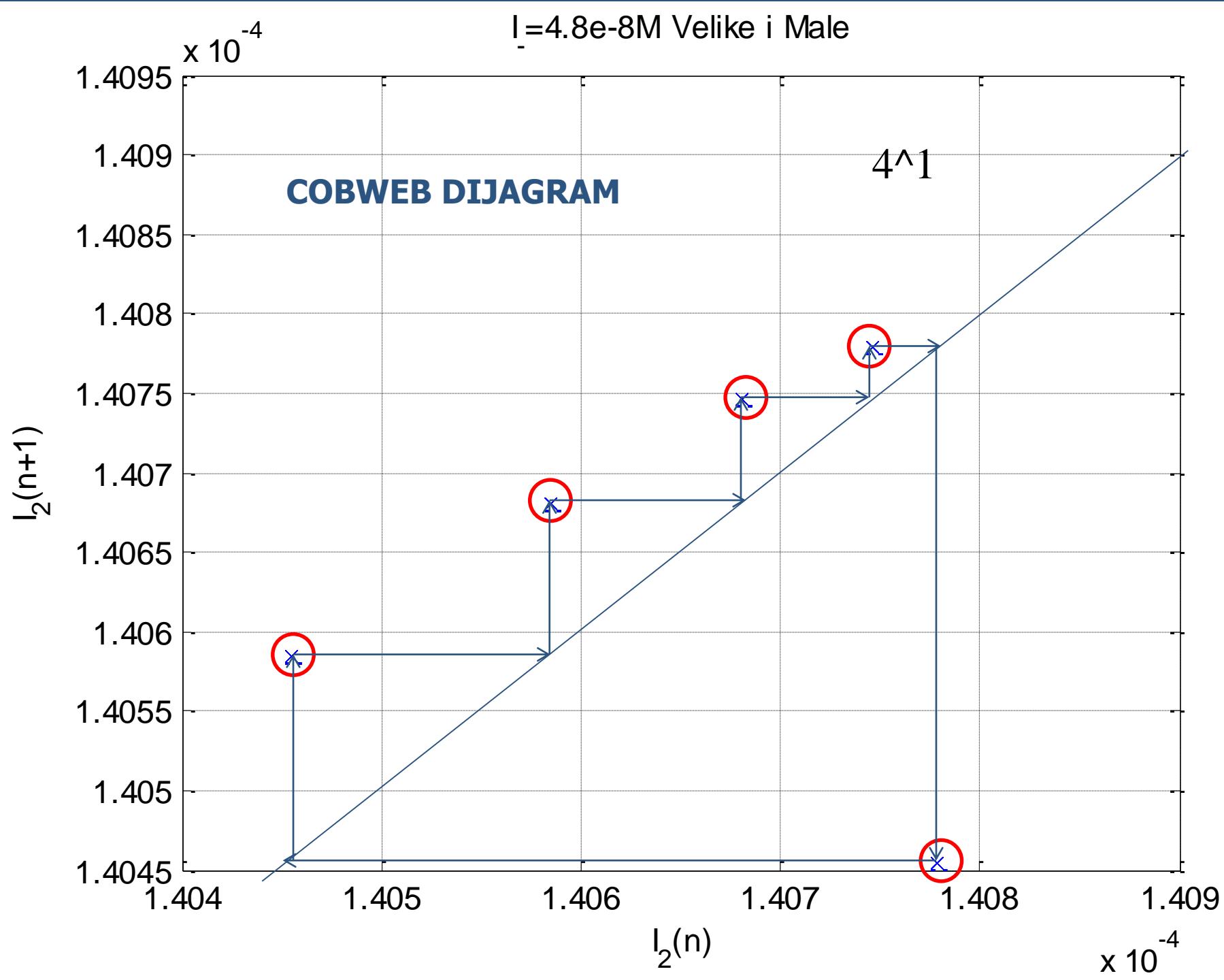
$I = 4.8 \times 10^{-8} M$  Velike i Male

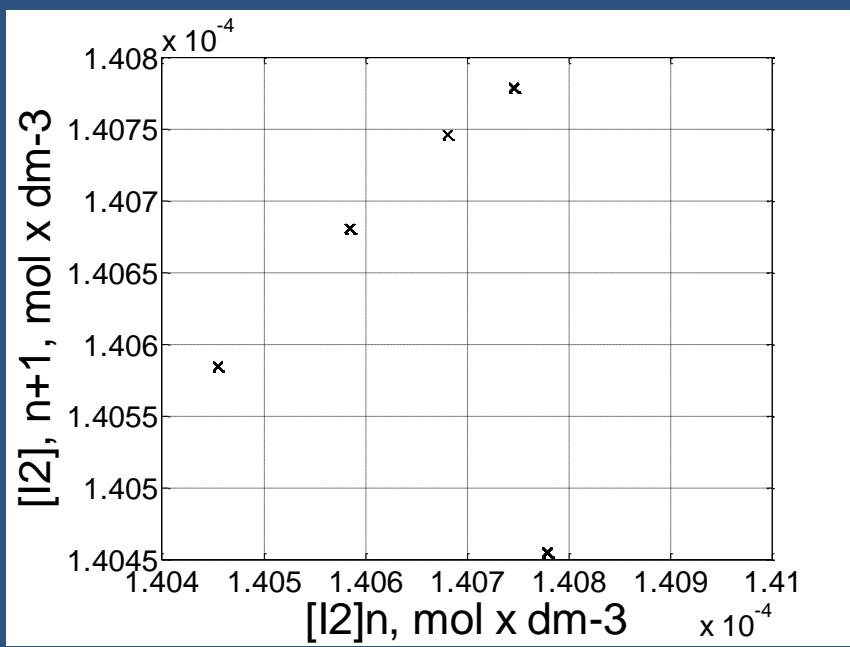


$I = 4.8 \times 10^{-8} M$  Velike i Male

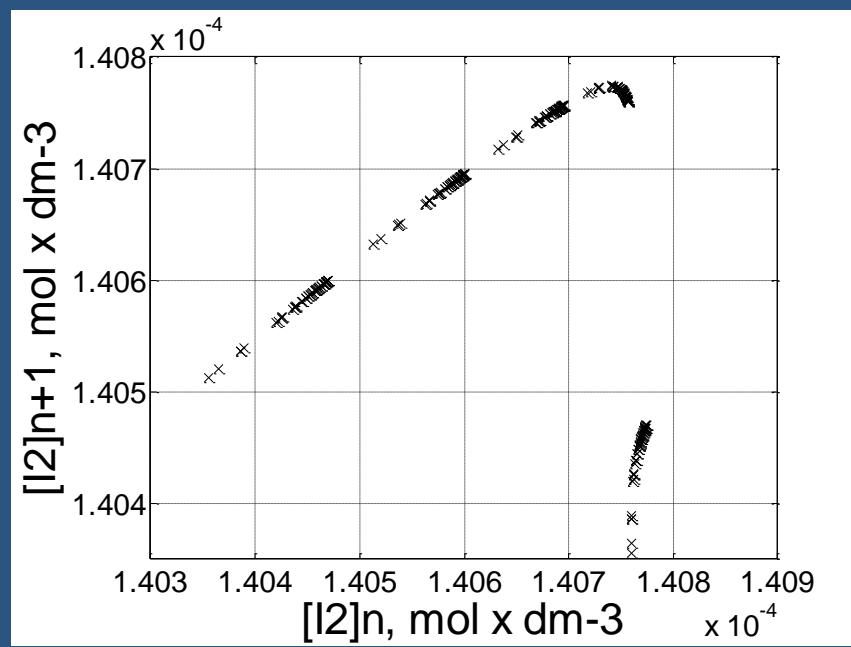


$I = 4.8 \times 10^{-8} M$  Velike i Male



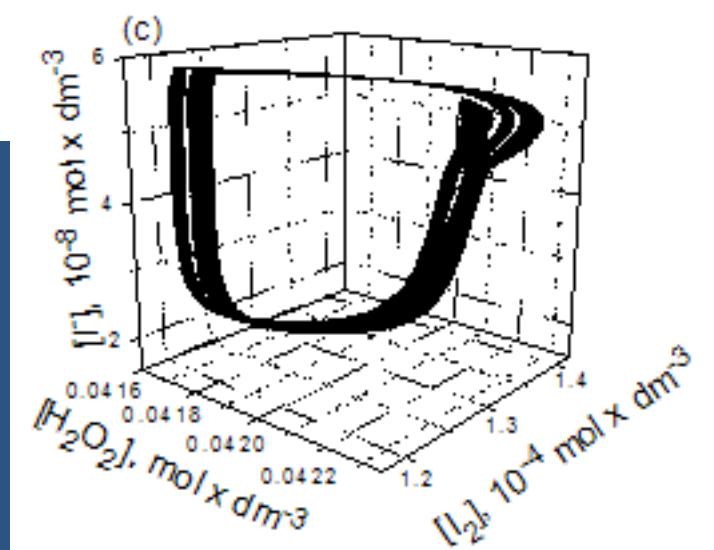
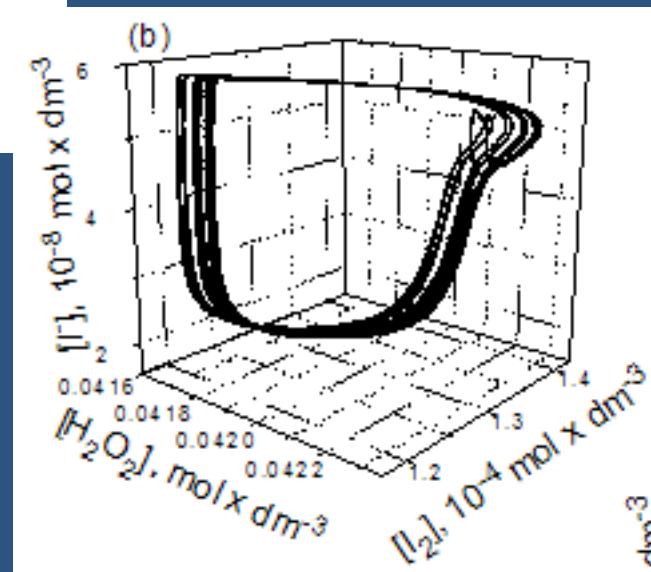
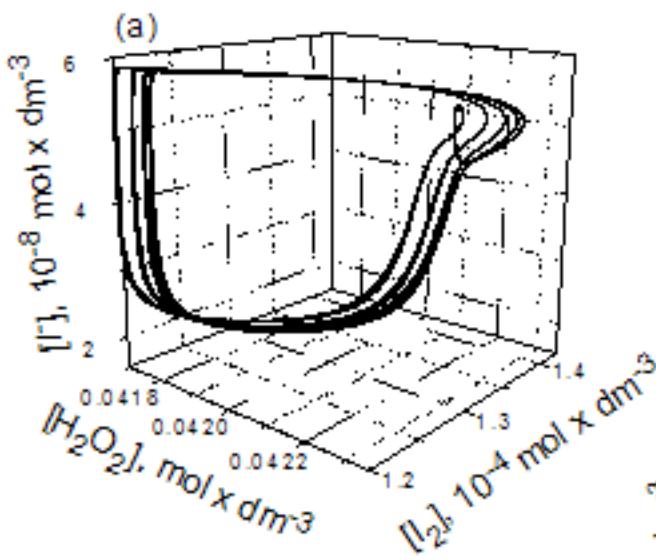


Periodika

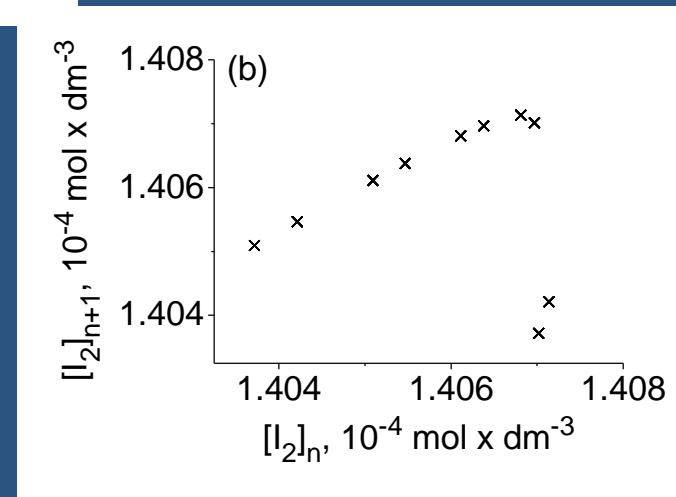
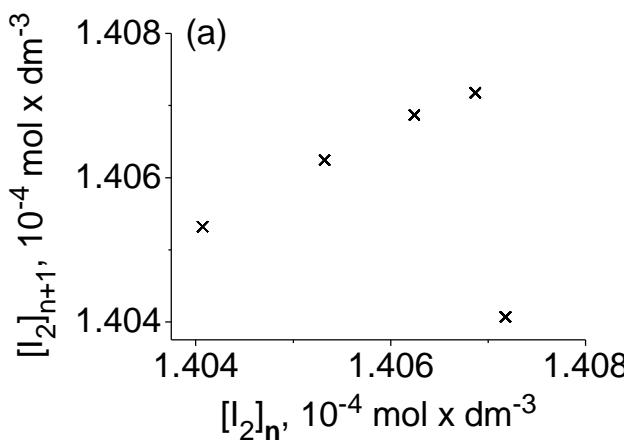


Haos

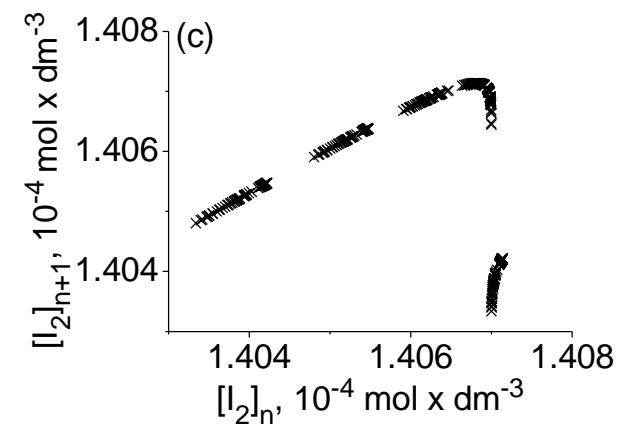
# Udvajanje perioda – scenario nastanka haosa



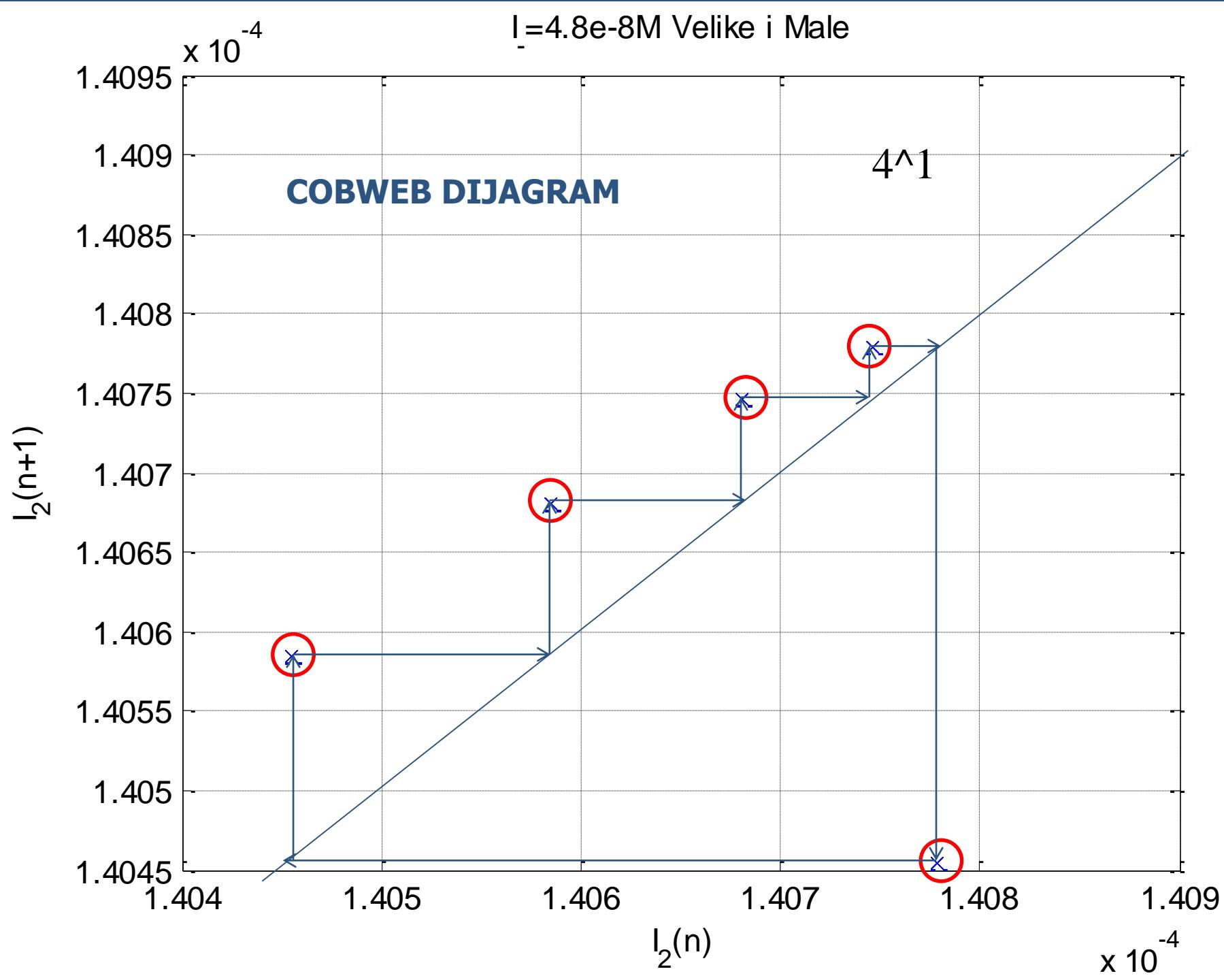
# Udvajanje perioda – scenario nastanka haosa



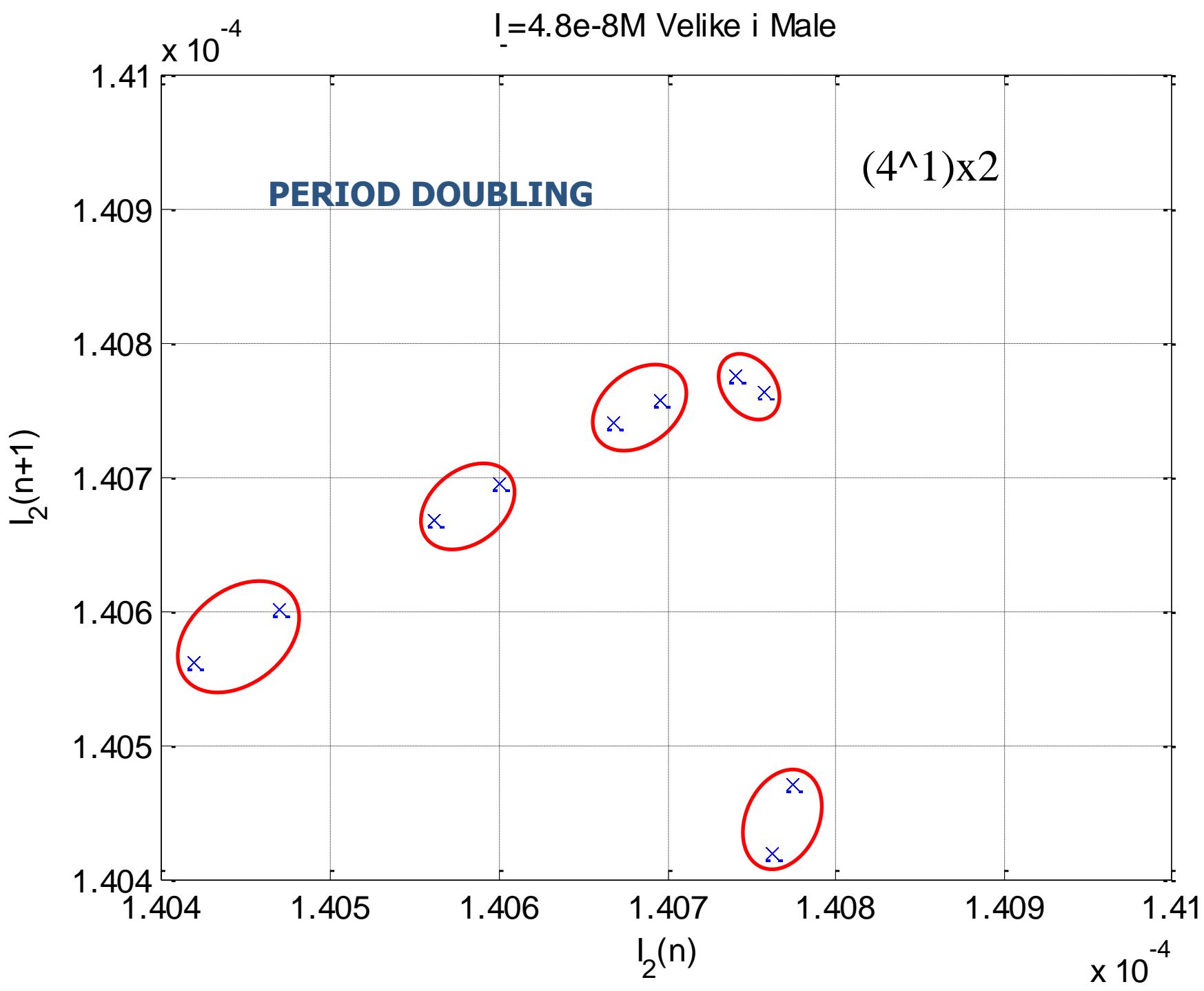
Prikaz Jednodimenzionih  
Mapa Poenkareovog preseka  
atraktora



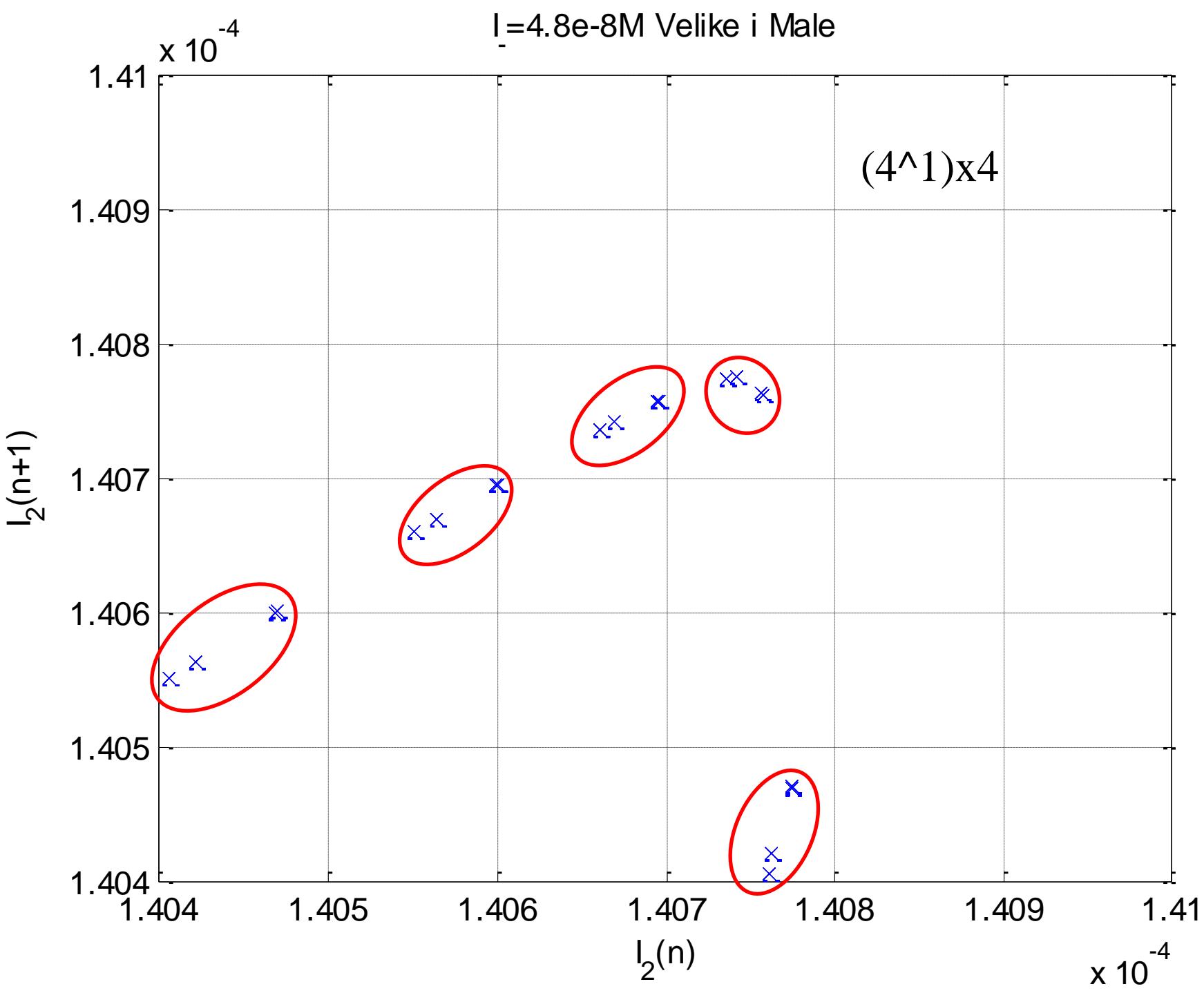
$I = 4.8 \times 10^{-8} M$  Velike i Male



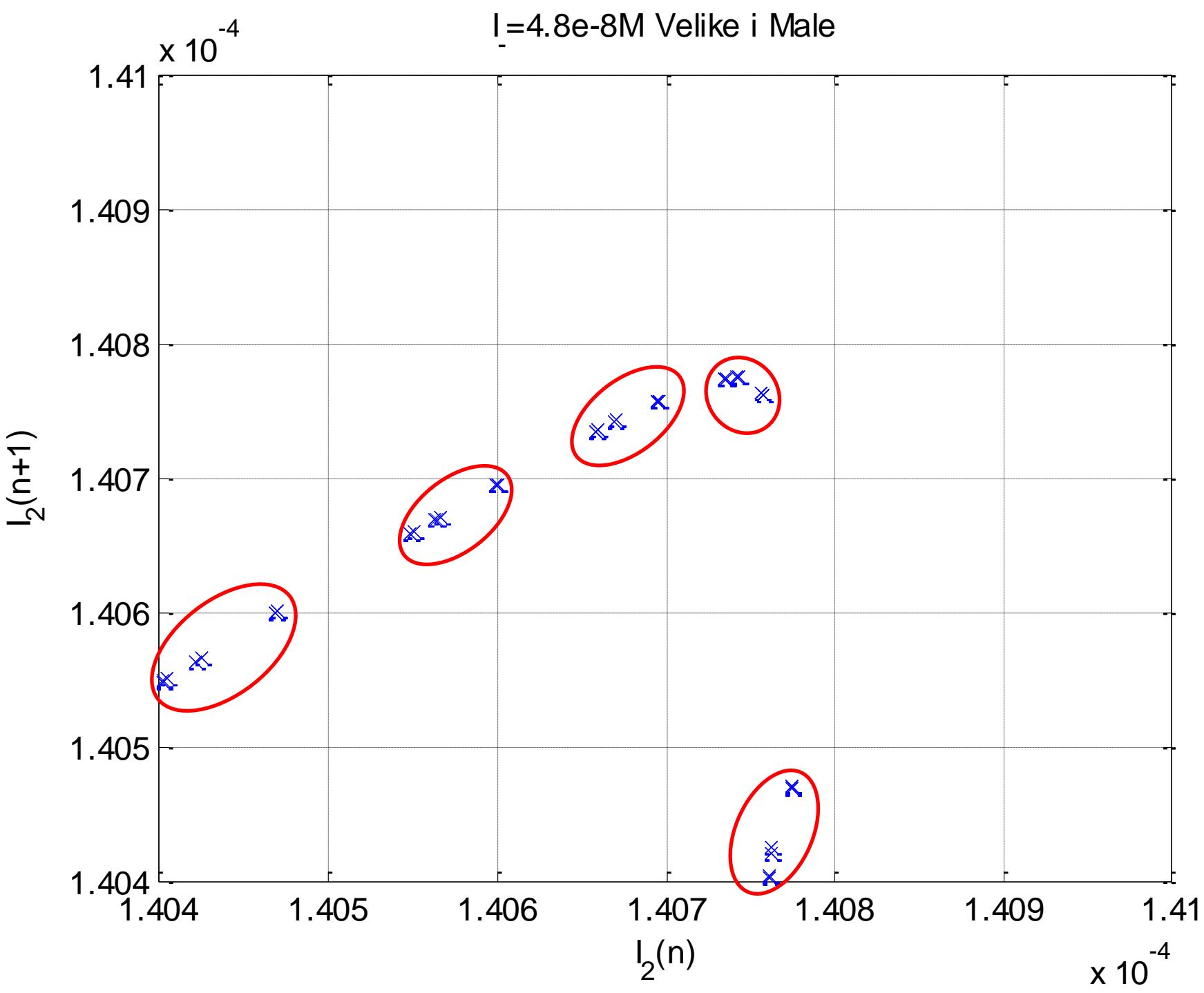
$I = 4.8 \times 10^{-8} M$  Velike i Male



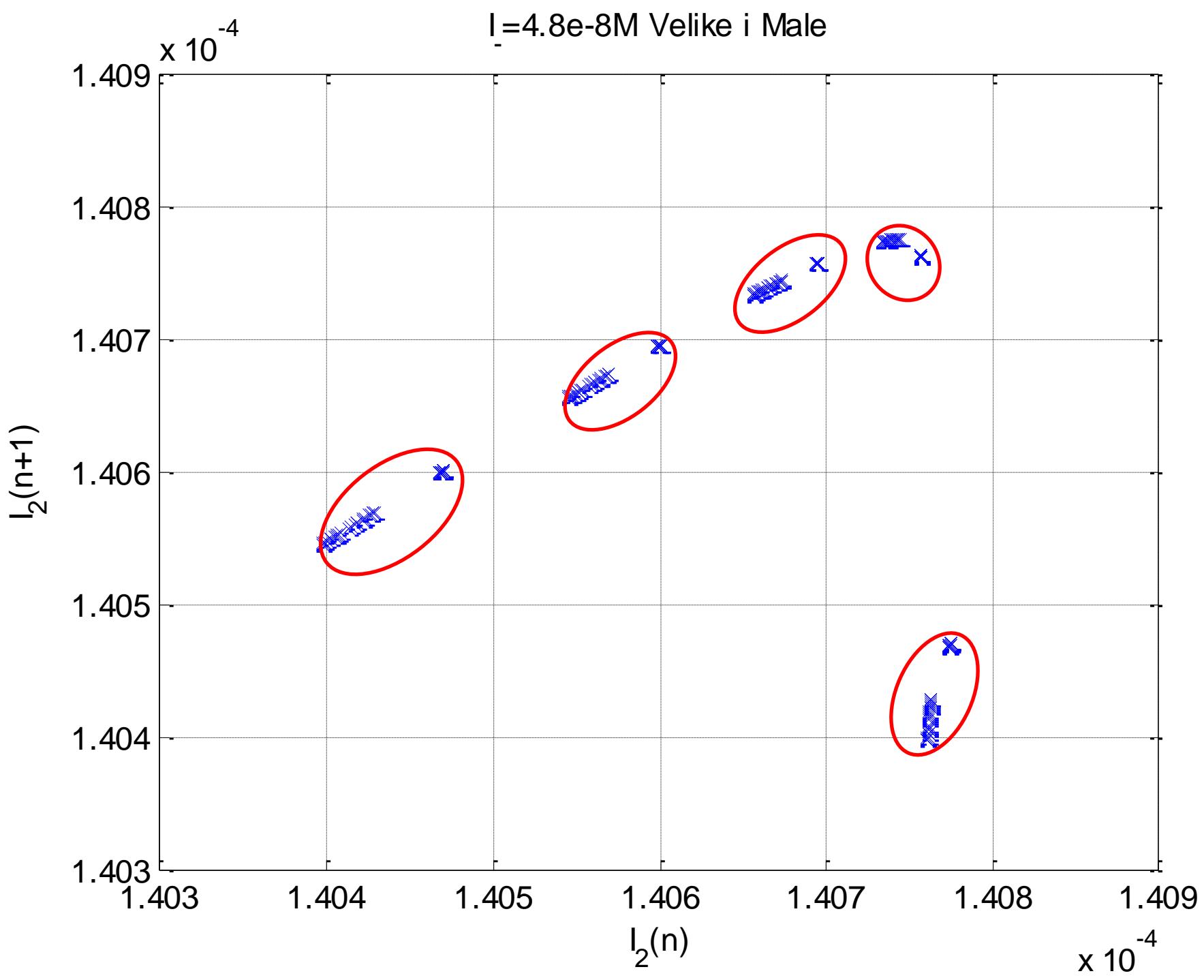
$I = 4.8 \times 10^{-8} M$  Velike i Male



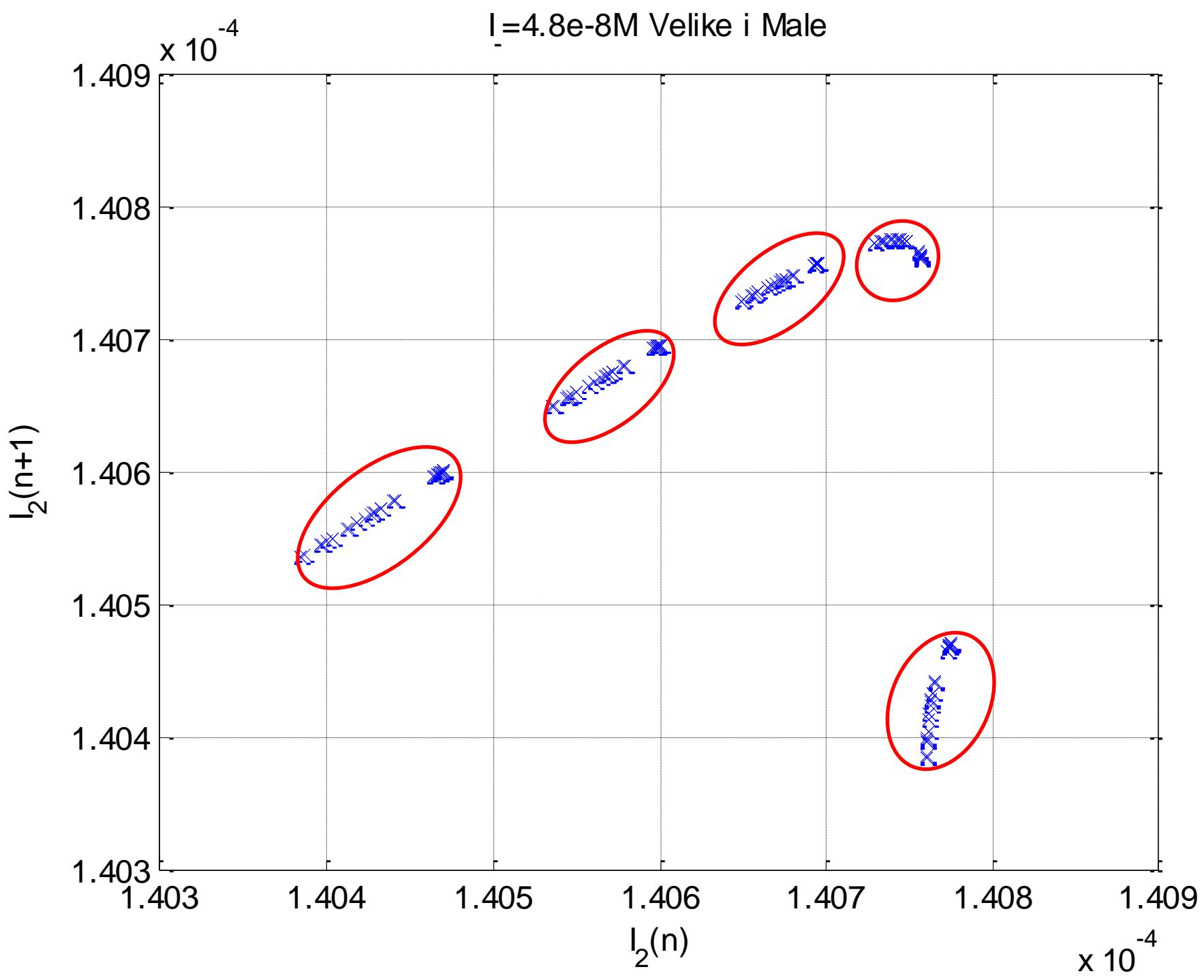
$I = 4.8 \times 10^{-8} M$  Velike i Male



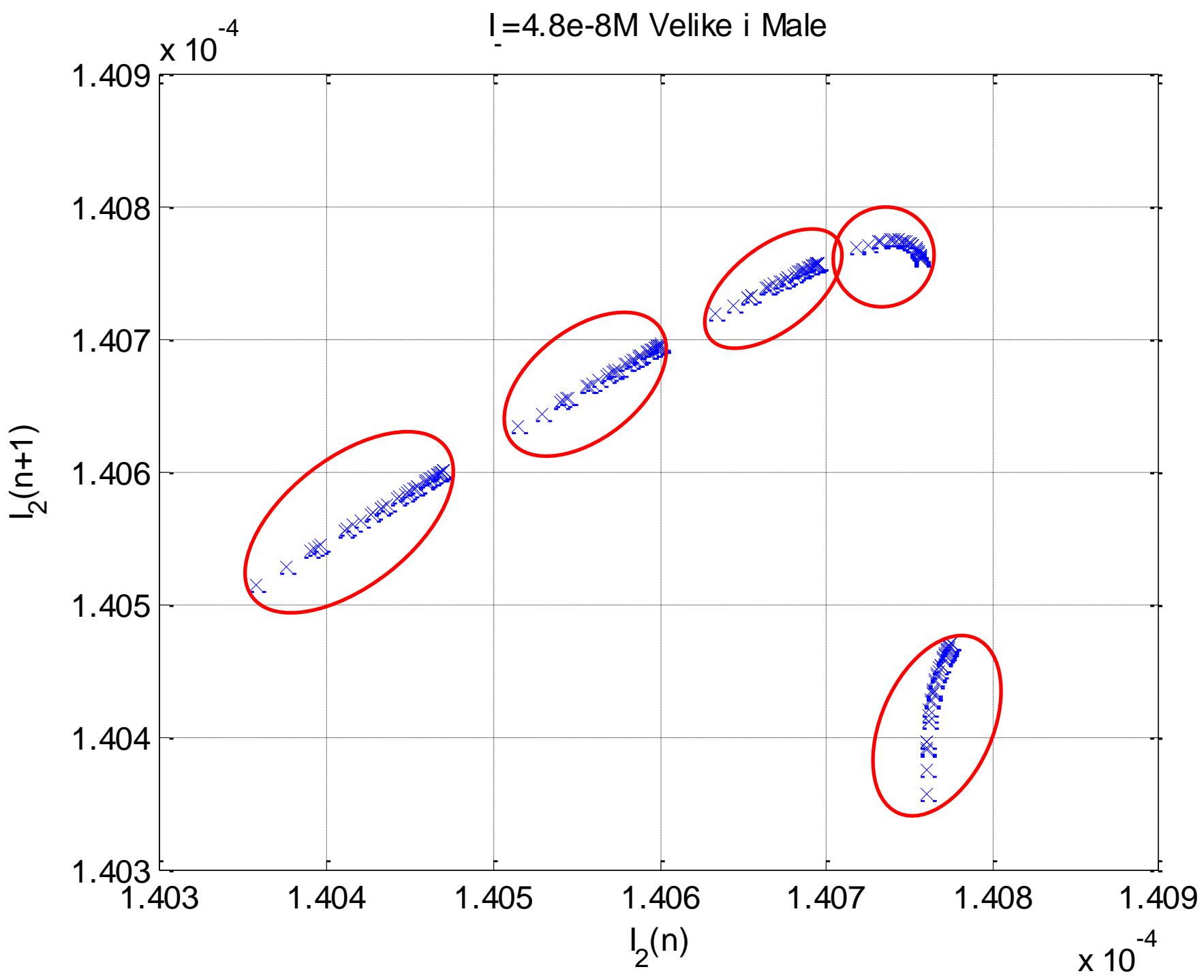
$I = 4.8 \times 10^{-8} M$  Velike i Male



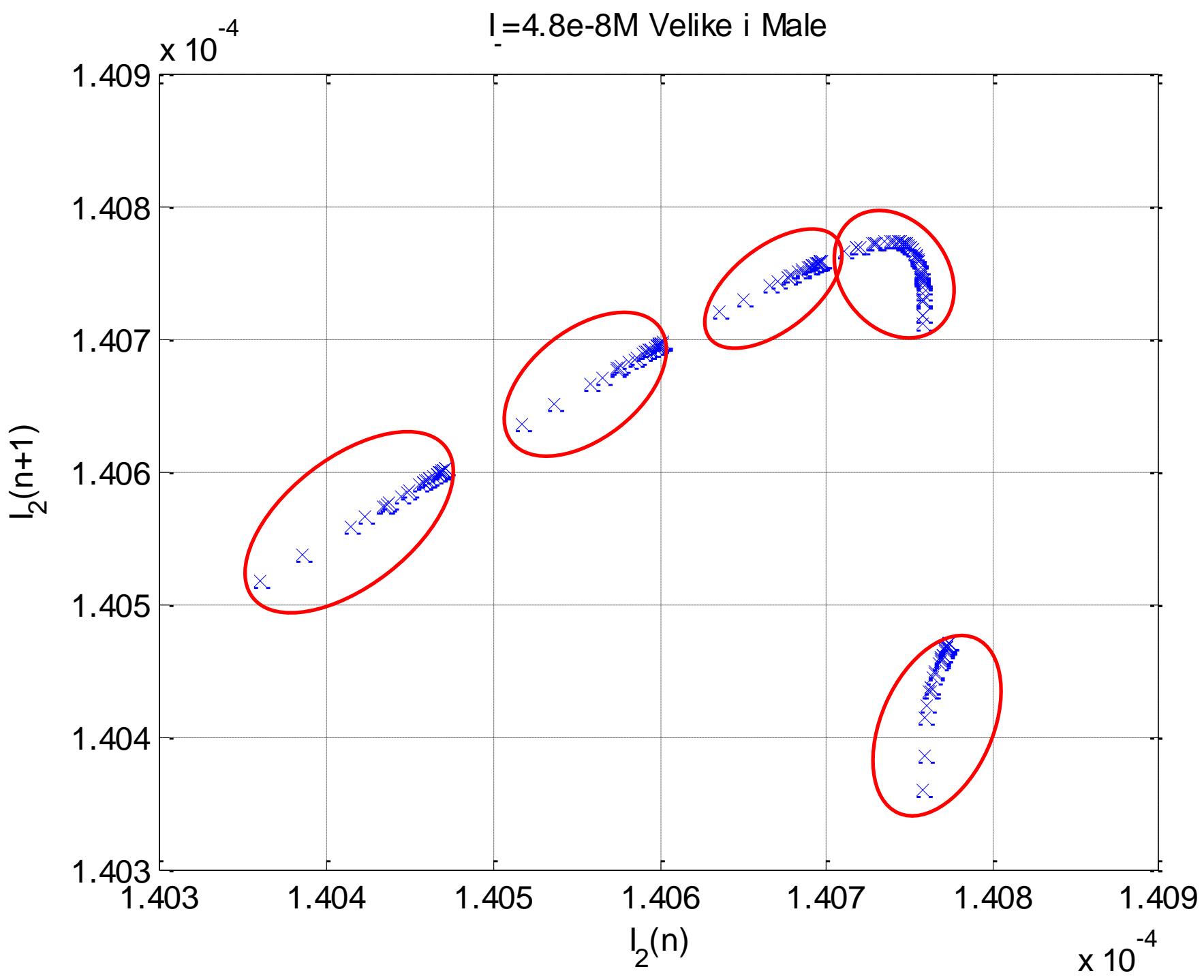
$I = 4.8 \times 10^{-8} M$  Velike i Male



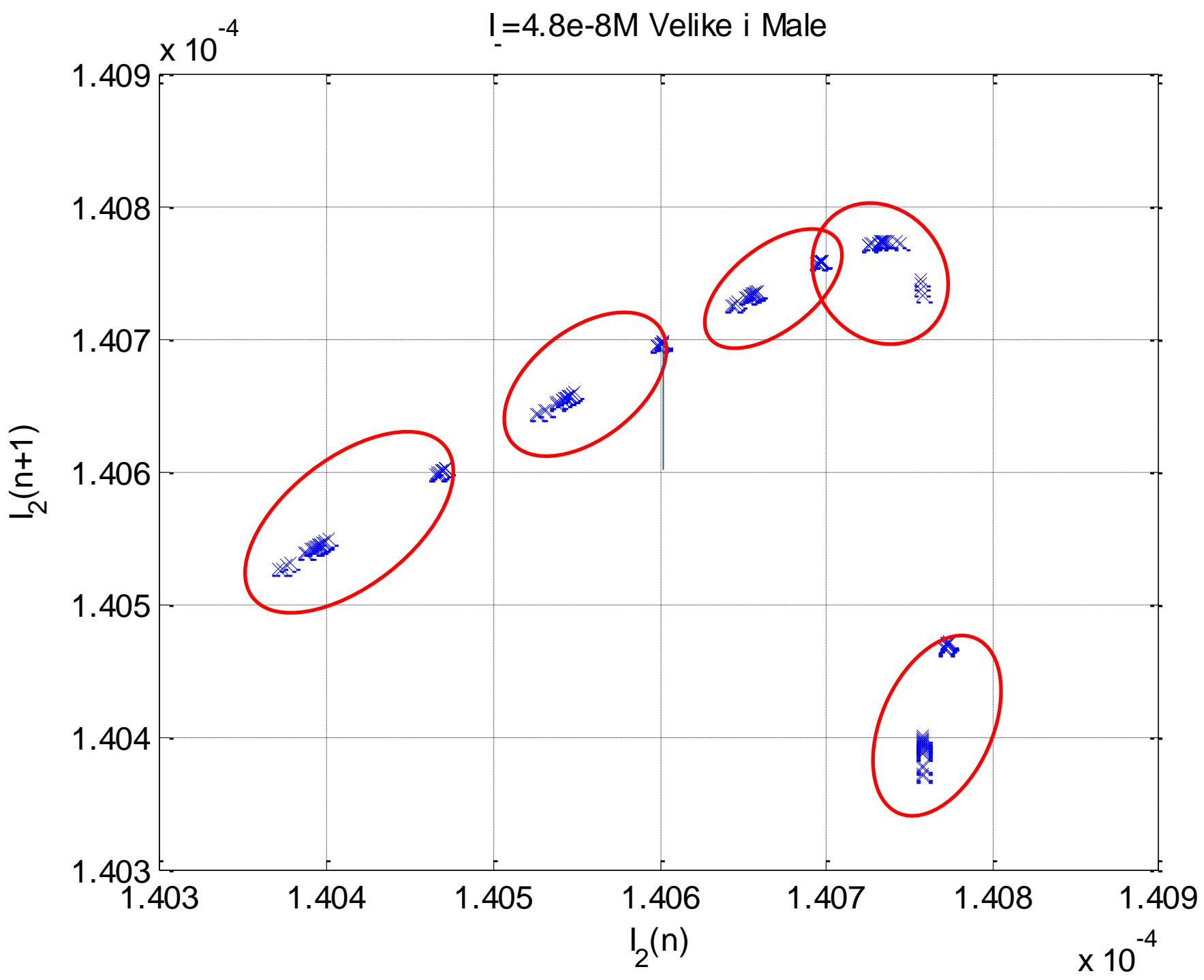
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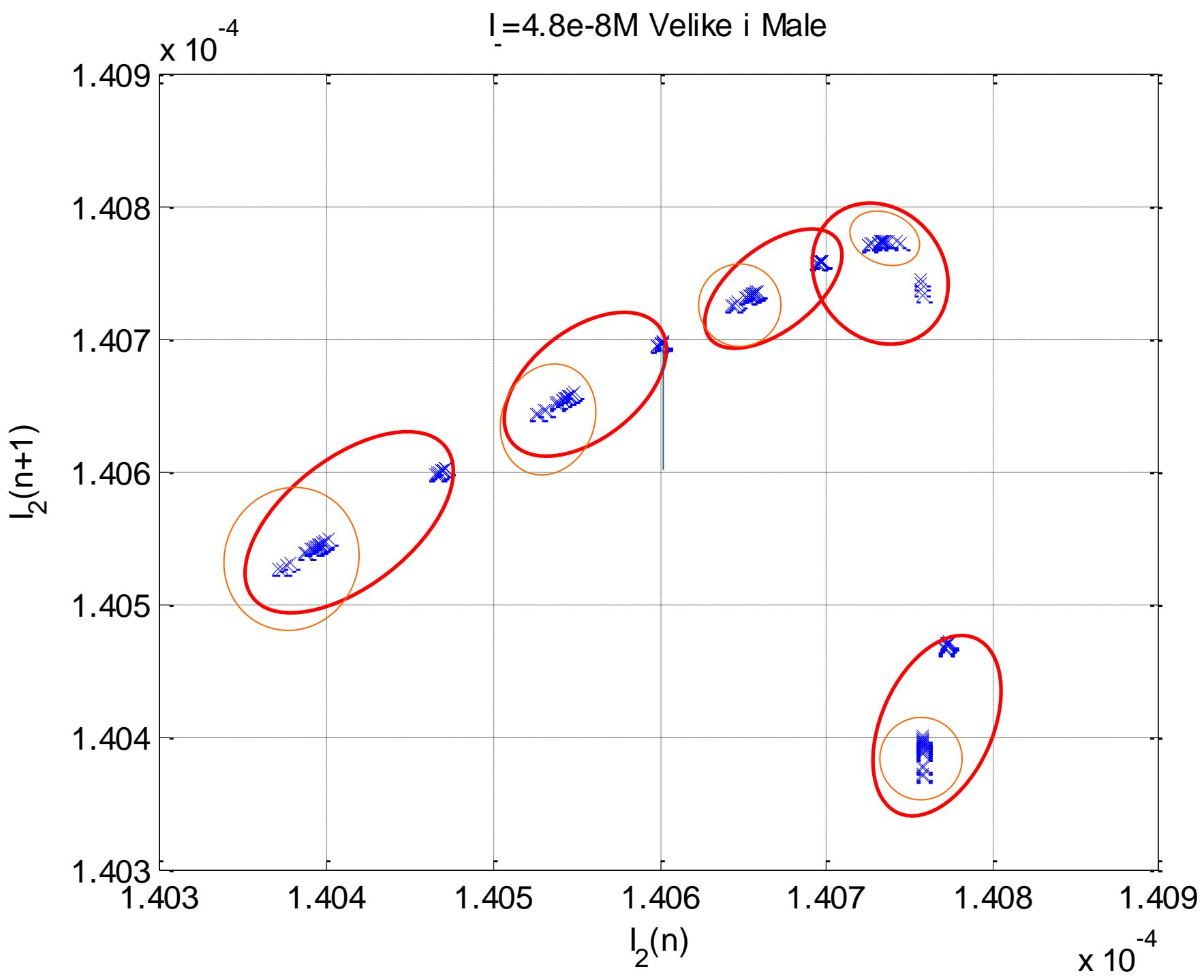
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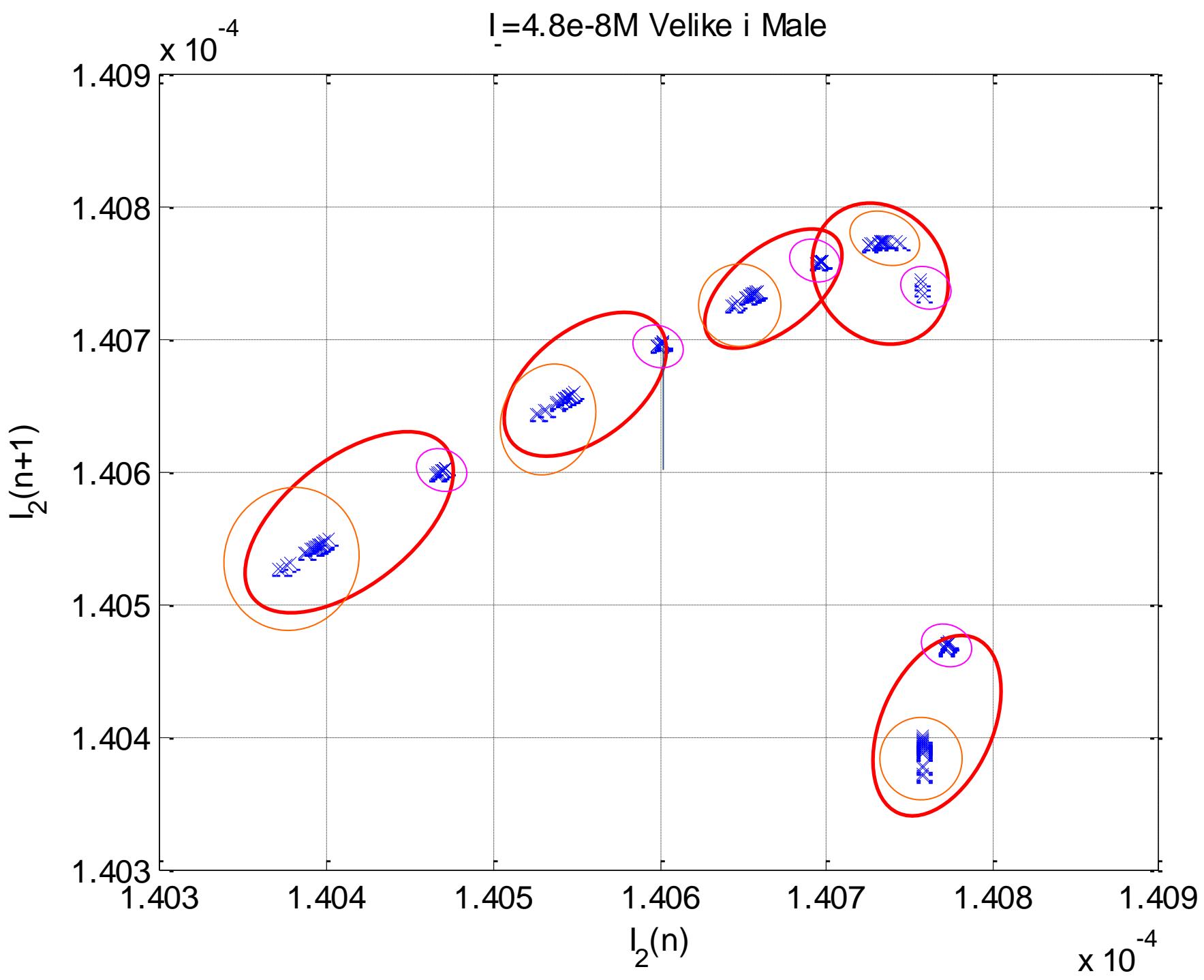
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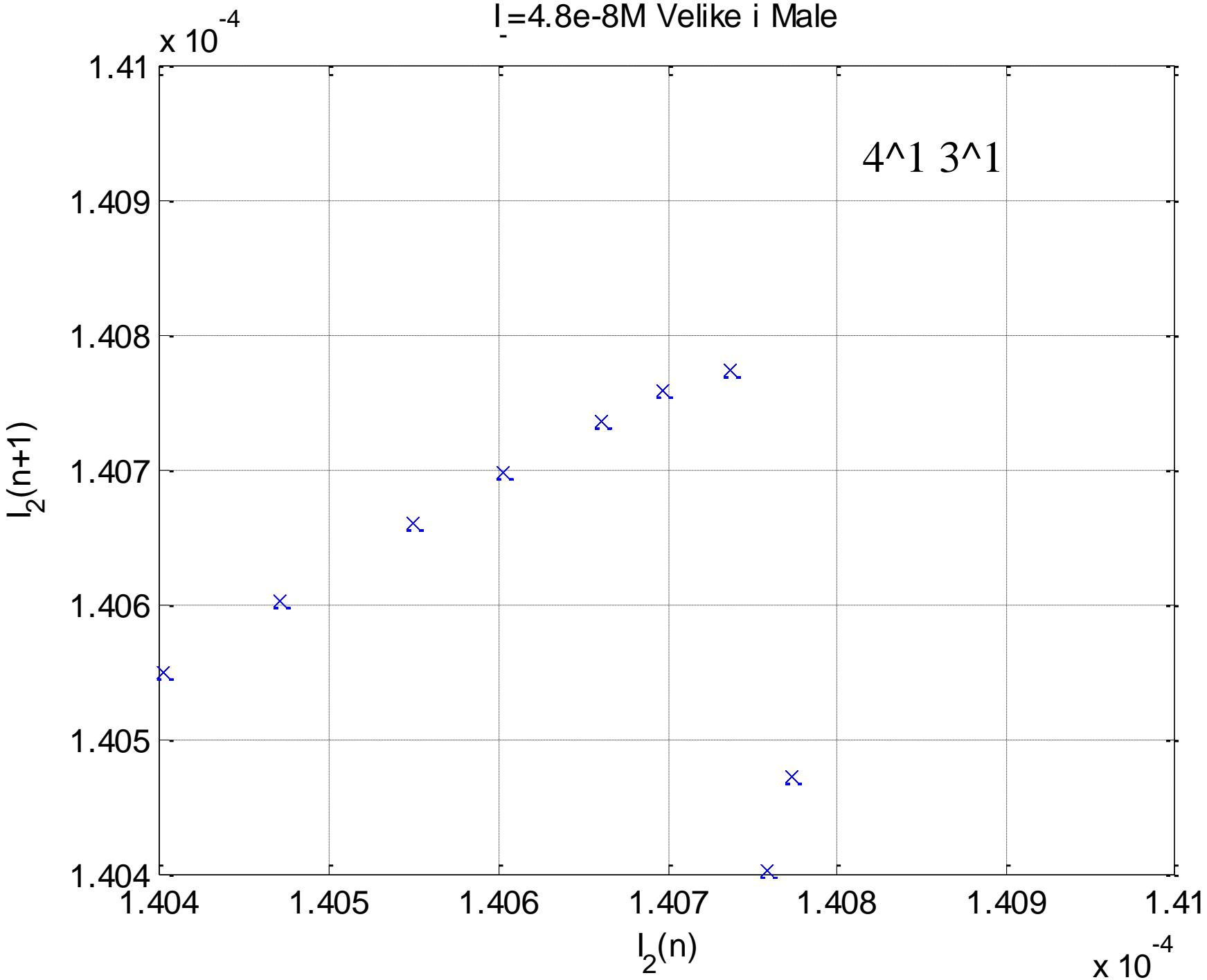
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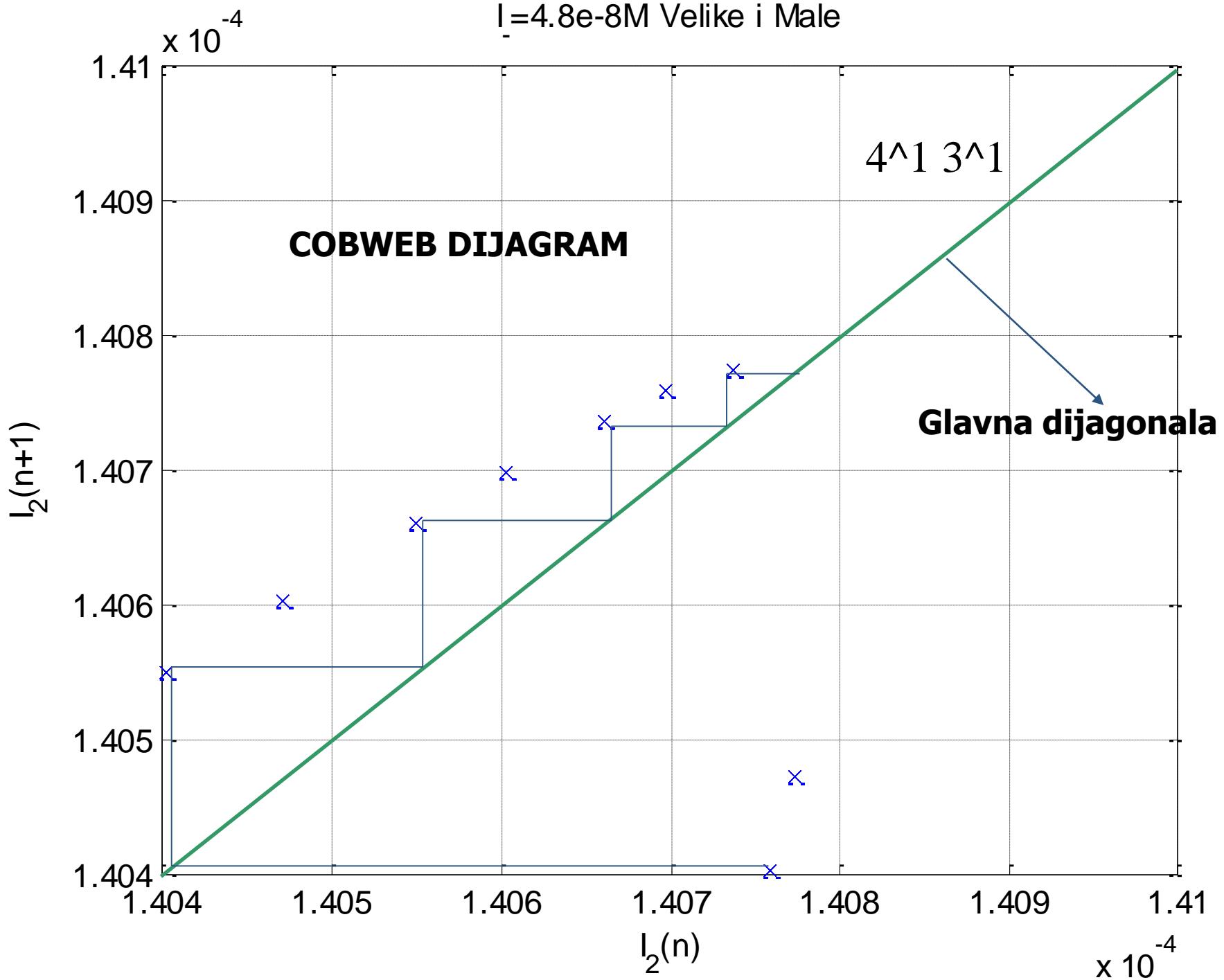
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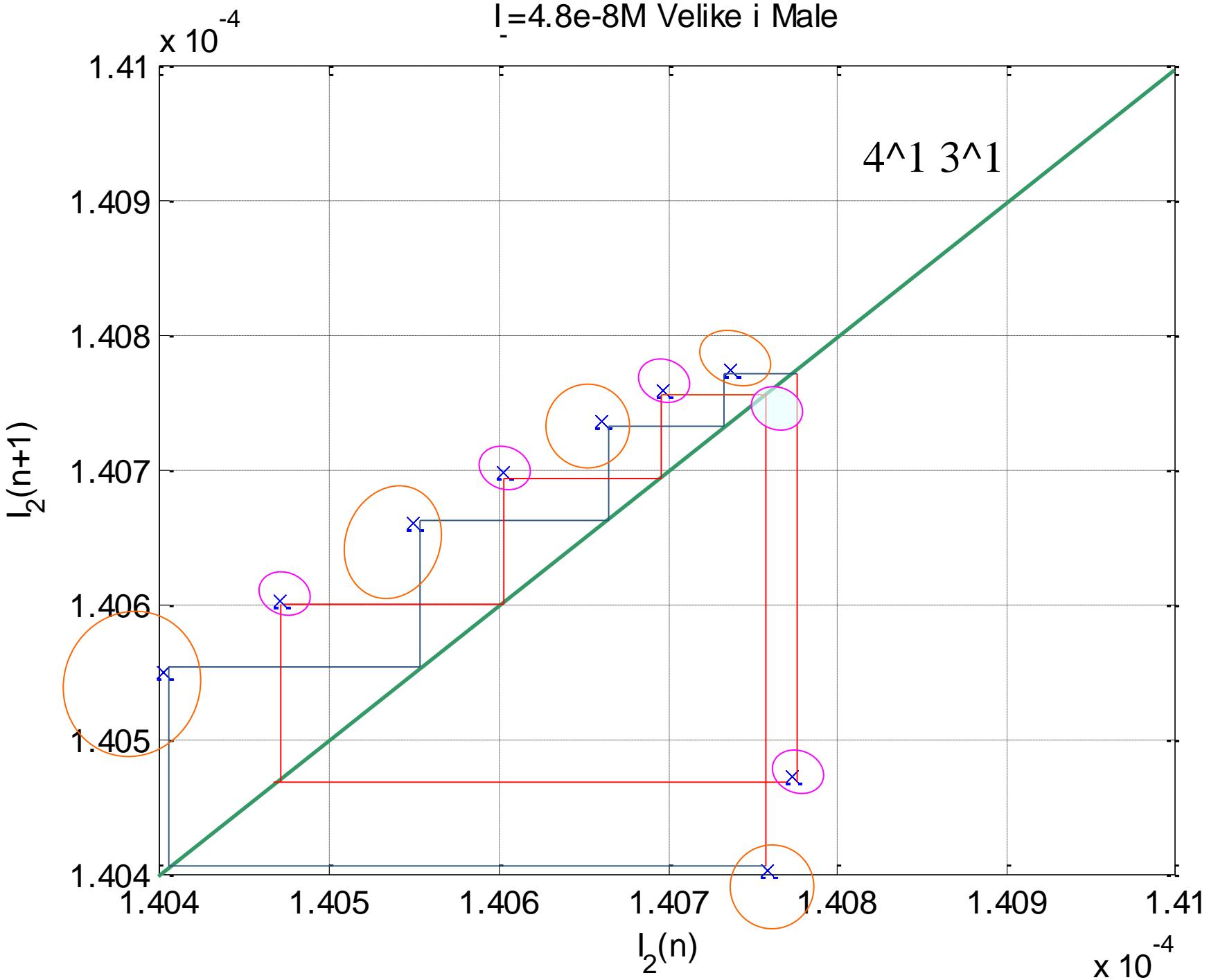
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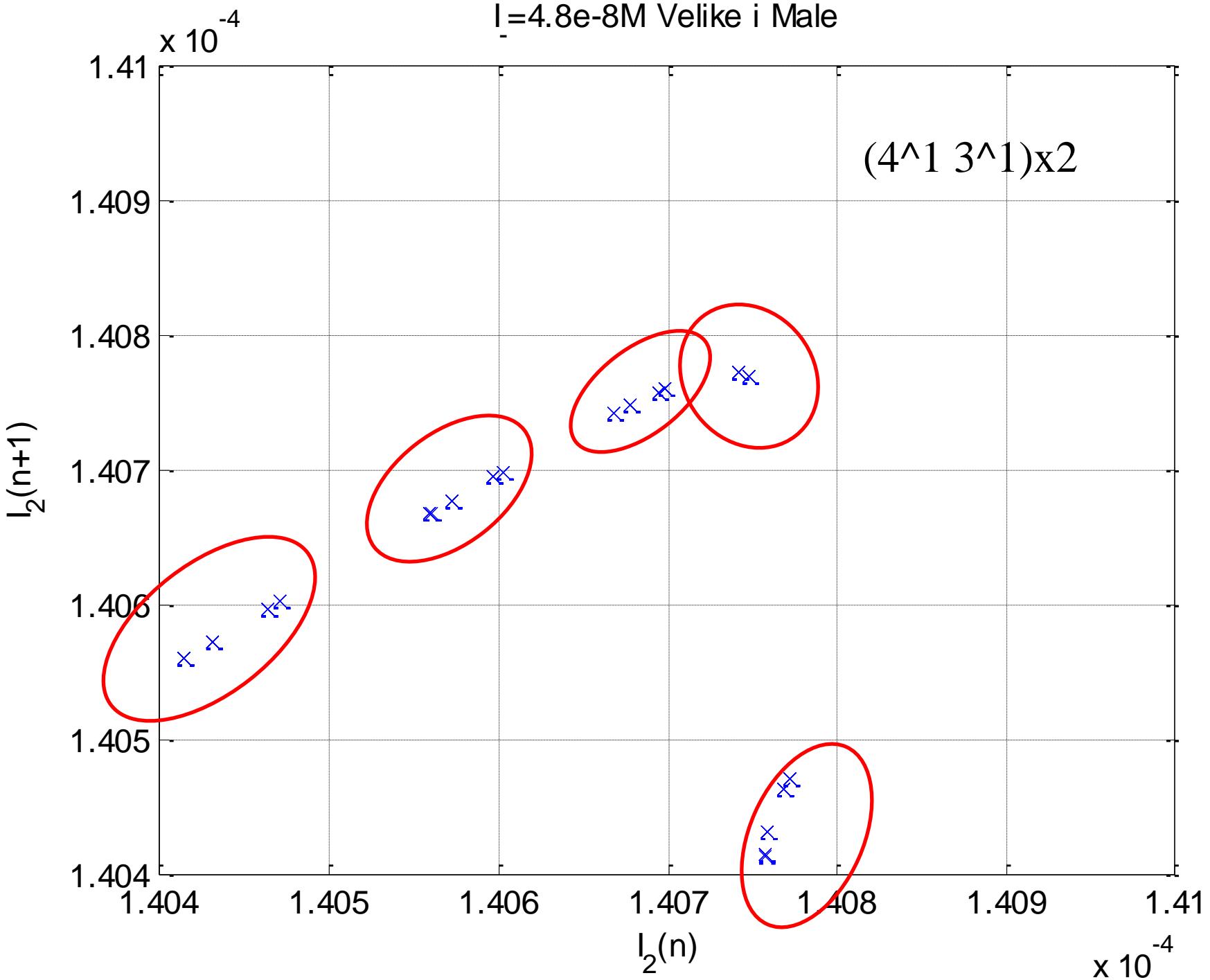
$I = 4.8 \times 10^{-8} M$  Velike i Male



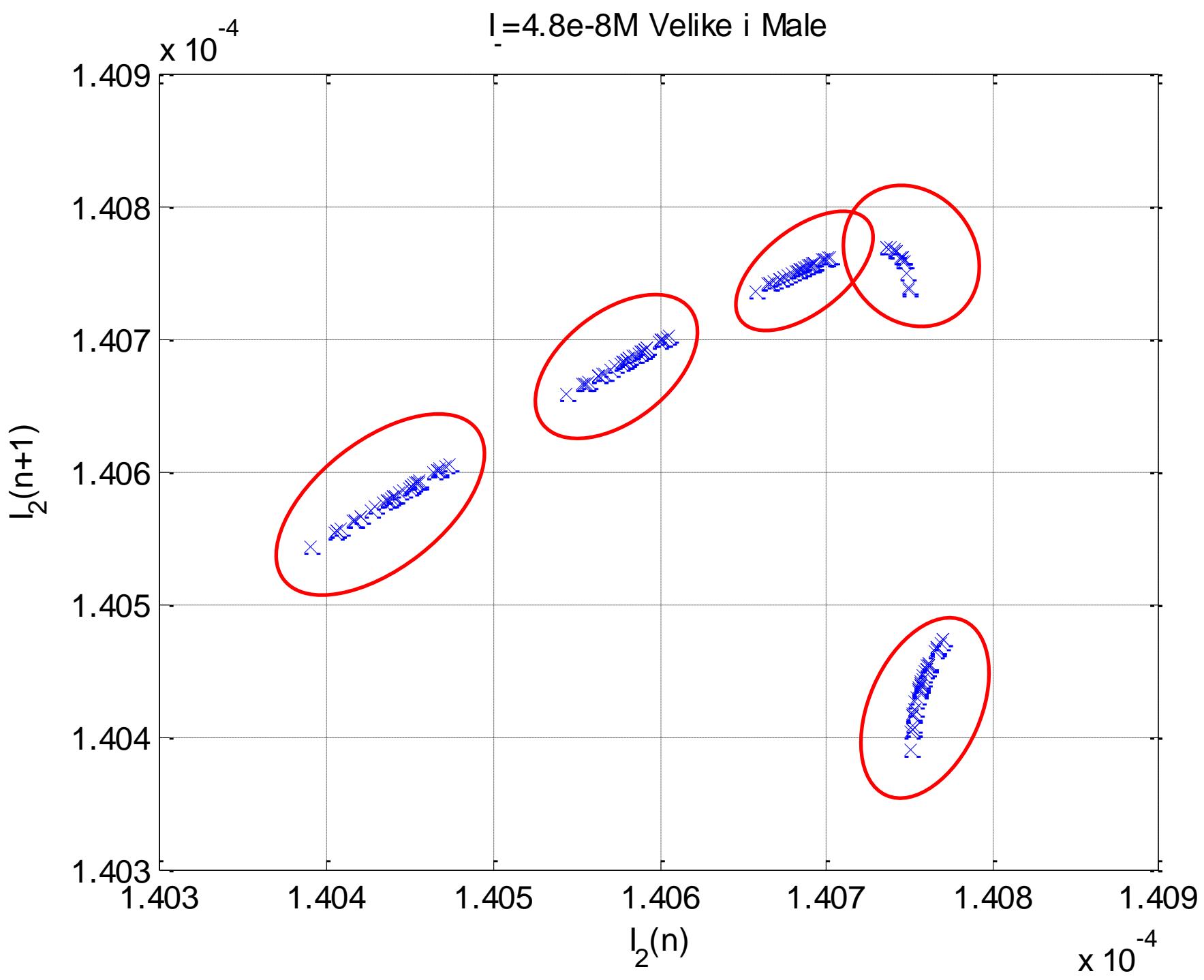
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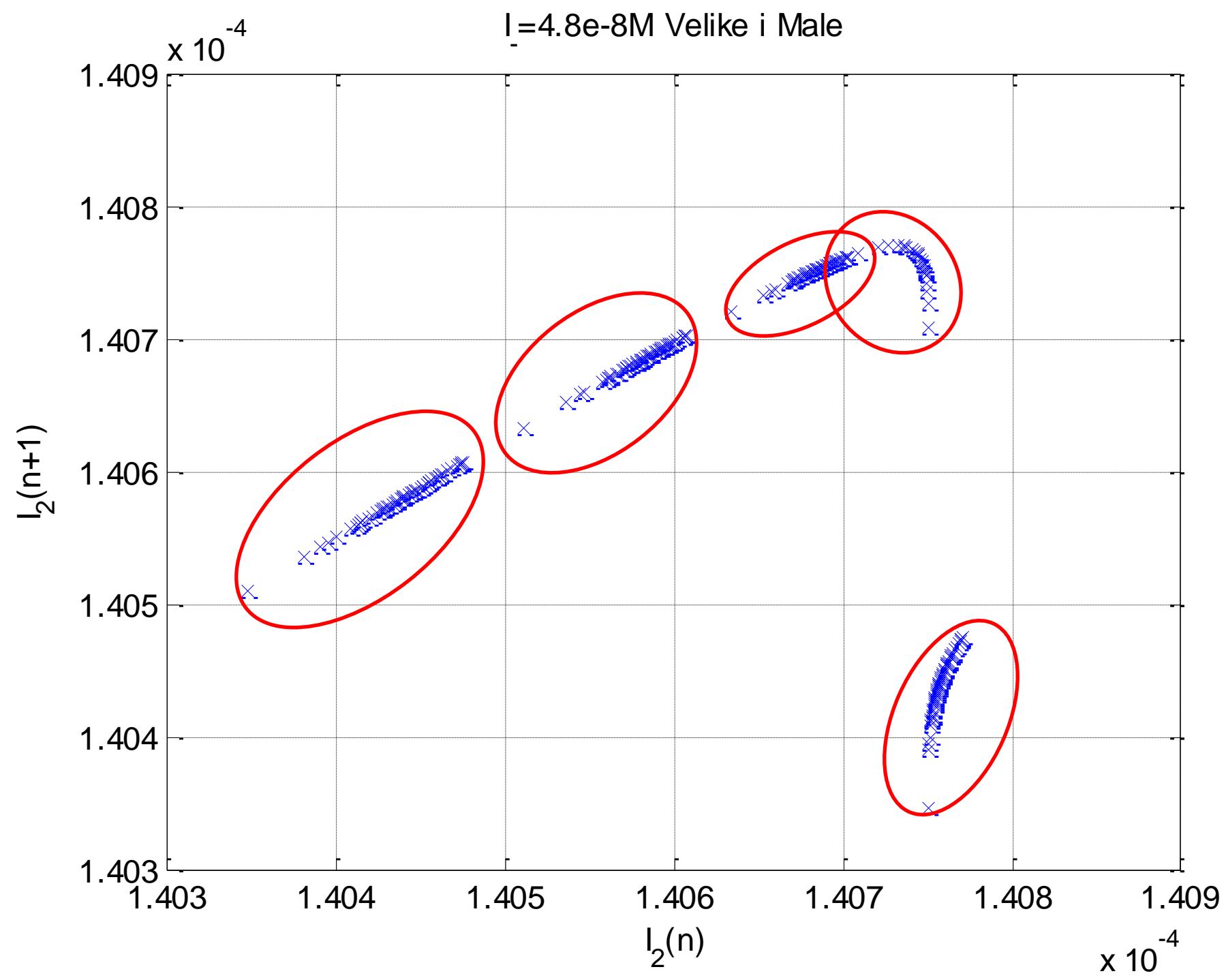
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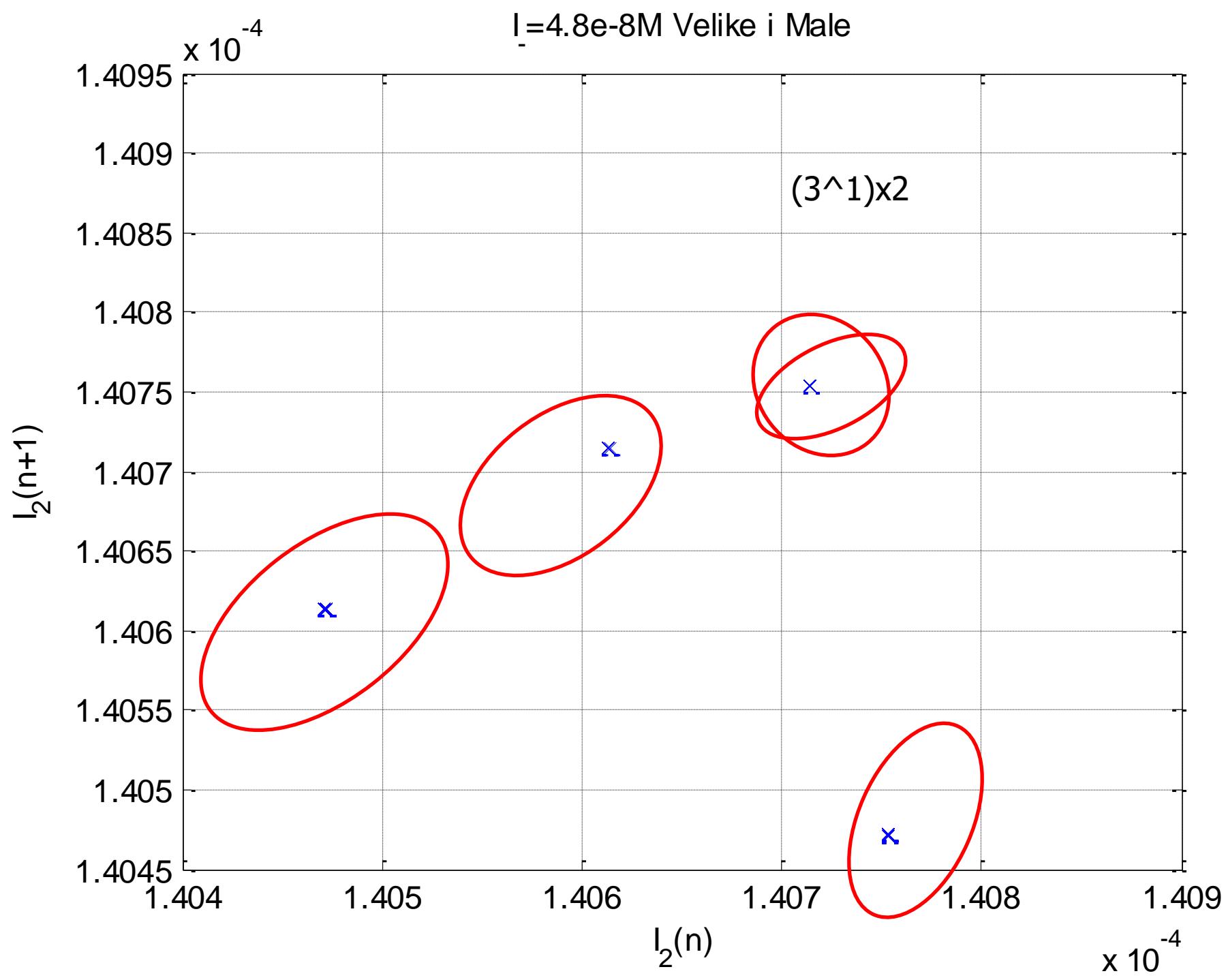
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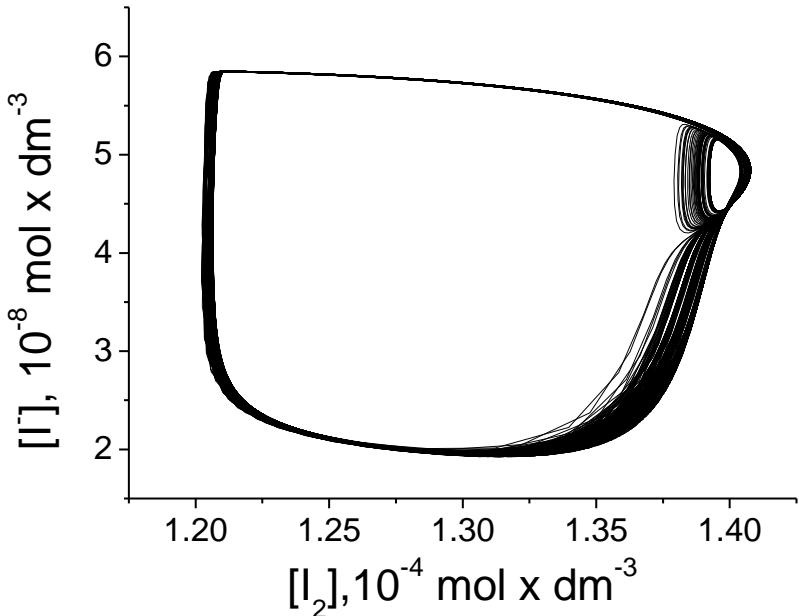


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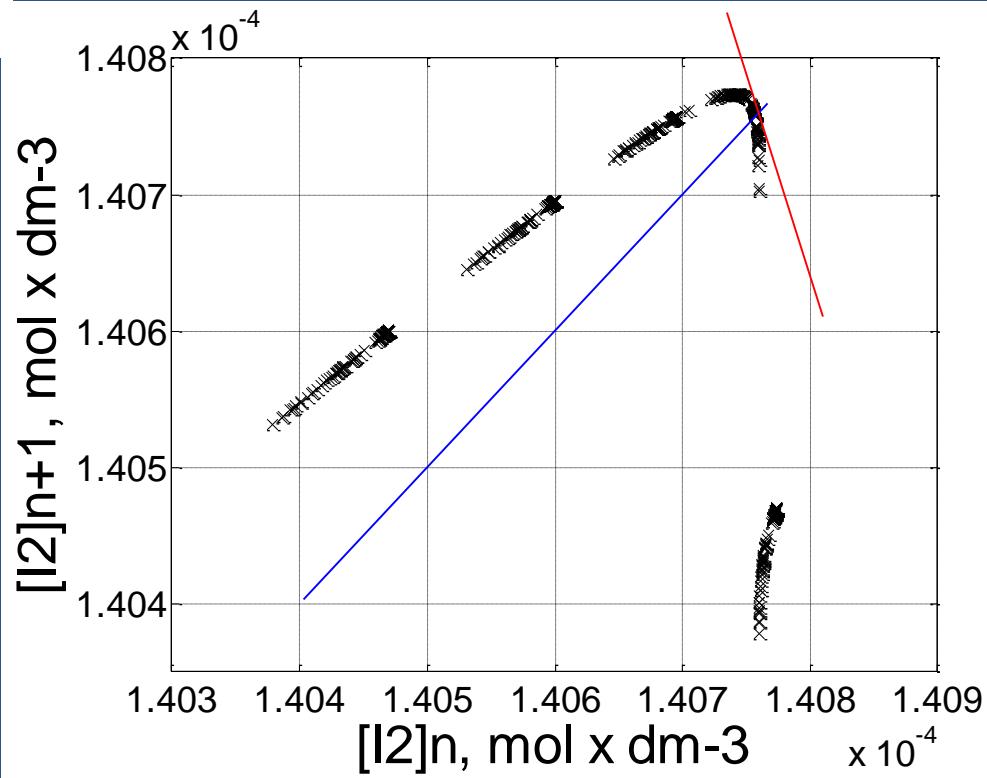


$$x_{n+1}^* = x_n^*$$

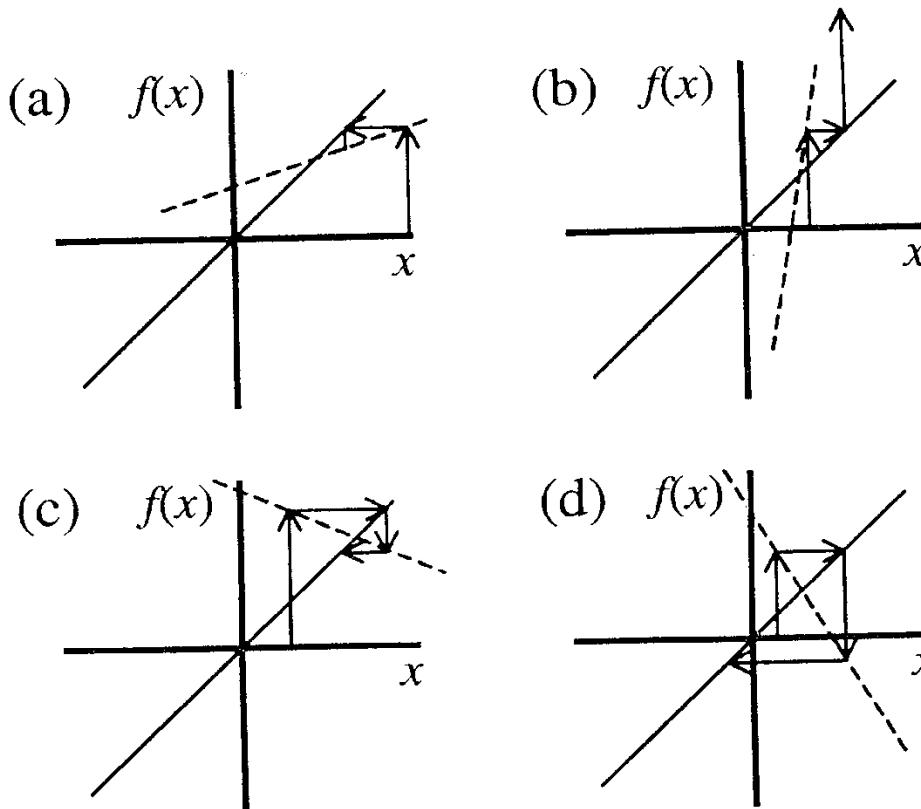
Nestabilna  
fiksna tačka

# Čudni atraktor

**FIKSNA TAČKA**



$$(x_{n+1} - x^*) = \left( \frac{df}{dx} \right)_{x^*} \cdot (x_n - x^*)$$



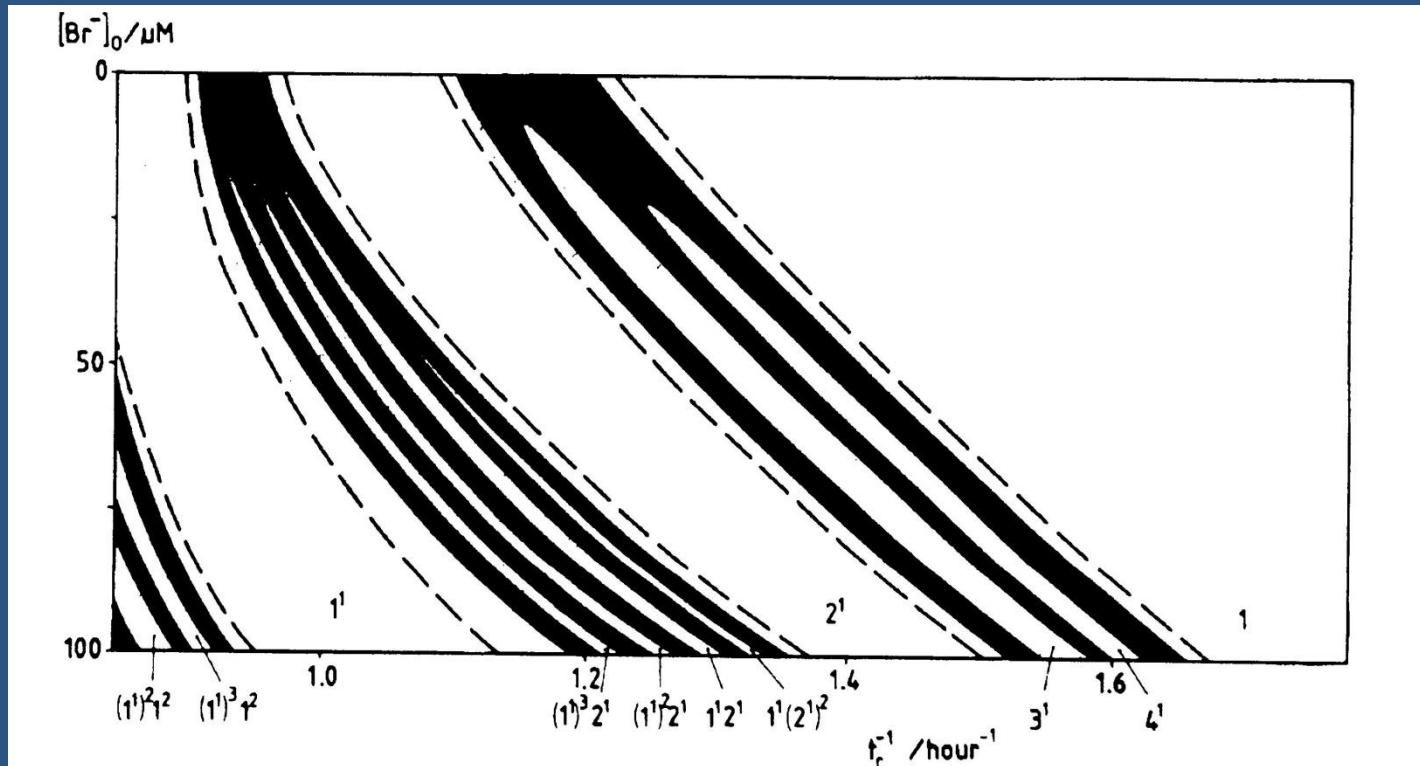
**Fig. 5.5.** A graphical representation of the effect of repeated use of map function  $f(x)$ . The map function is plotted as a dashed line. The  $f(x) = x$  line is solid. (a)  $0 < df/dx < 1$  gives a stable fixed point. (b)  $df/dx > 1$  gives an unstable fixed point. (c)  $-1 < df/dx < 0$  gives a stable fixed point. (d)  $df/dx < -1$  gives an unstable fixed point. Note that when  $df/dx < 0$ , the successive iteration points alternate from one side of the fixed point to the other.

In Chapter 2, we used a Taylor series expansion near  $x^*$  to arrive at the same

# Klasifikacija mehanizma oscilatora na osnovu bifurkacionih dijagrama (SNA) - Polazna ideja

J. Phys. Chem. 1989, 93, 2796-2800

Use of Bifurcation Diagrams as Fingerprints of Chemical Mechanisms  
Zoltan Noszticzius, William D. McCormick, and Harry L. Swinney



Mnogo više o ispitivanju dinamike složenih reakcionih sistema,  
može se naći u knjizi:

*Ljiljana Kolar-Anić, Željko Čupić, Vladana Vukojević, Slobodan Anić*  
**Dinamika nelinearnih procesa**

(Fakultet za fizičku hemiju, Univerzitet u Beogradu, Beograd 2011)

# Hvala na pažnji.

Apstrakte na jednoj strani slati na adresu:  
[zcupic@ihtm.bg.ac.rs](mailto:zcupic@ihtm.bg.ac.rs)  
do [25.03.](#)