

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. Metode ispitivanja dinamike složenih reakcionih sistema

Sadržaj II časa

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

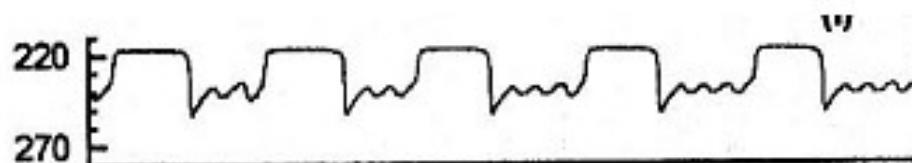
Sadržaj II časa

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 - Fiksna tačka

Vremenske serije

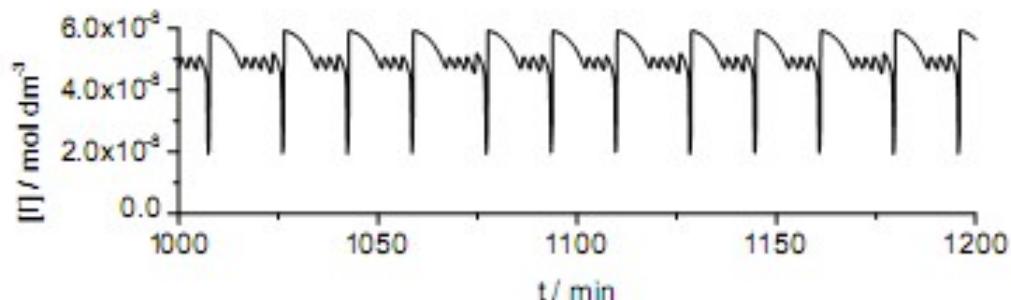
BL reakcije u dobro mešajućem **otvorenom** reaktoru.

Eksperimentalna ispitivanja



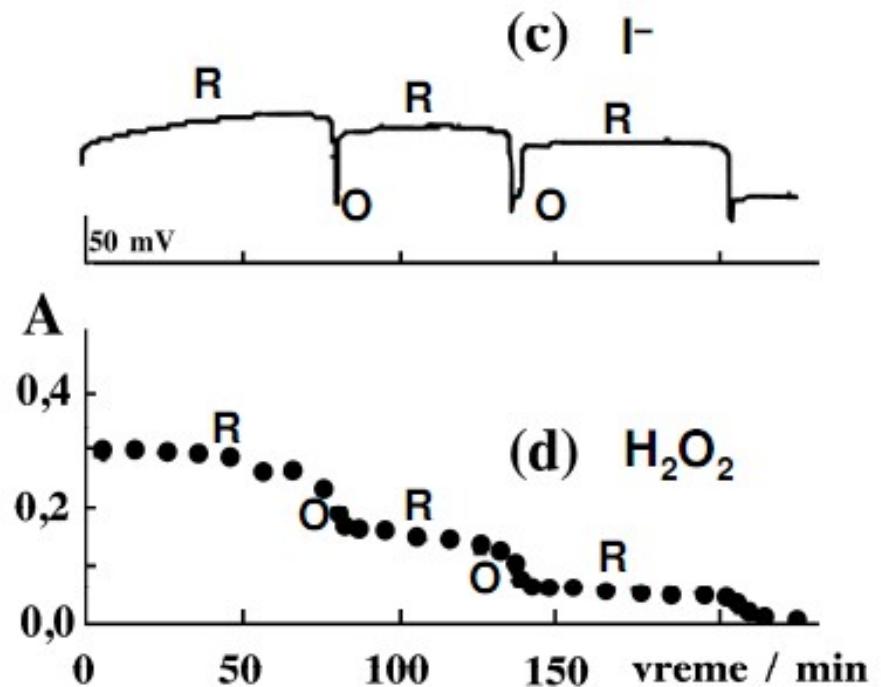
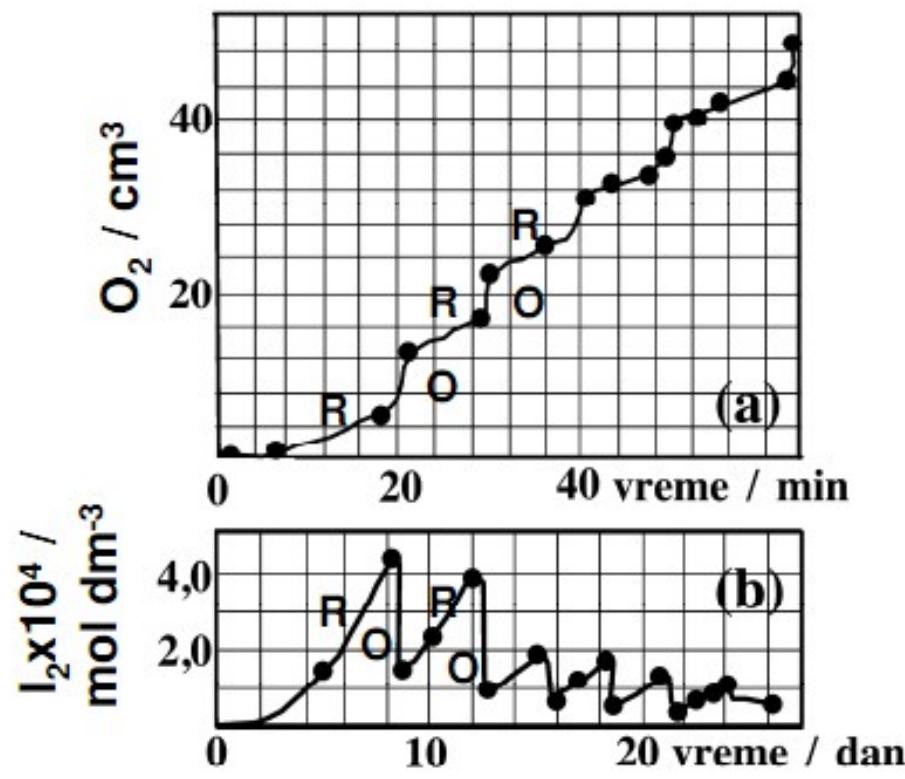
Vukojević, V.; Anić, S.; Kolar-Anić, Lj. *J. Phys. Chem. A* 2000, 104, 10731.

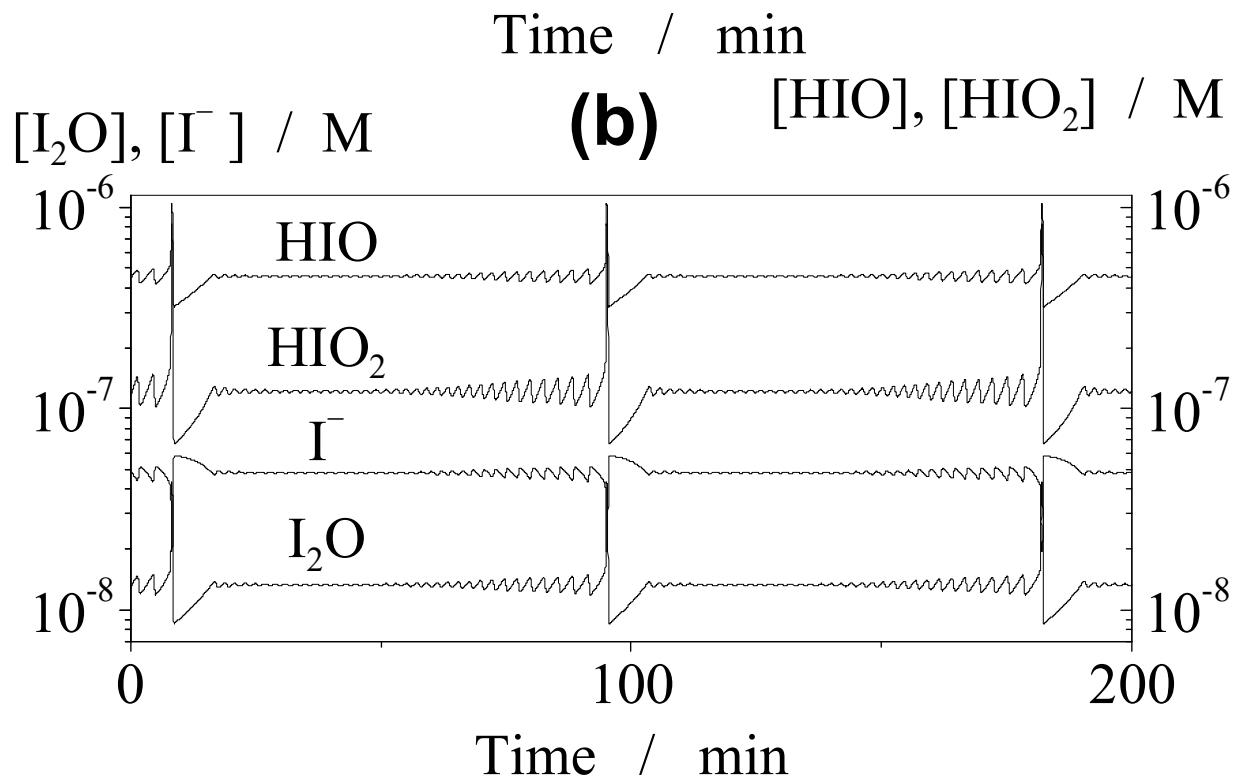
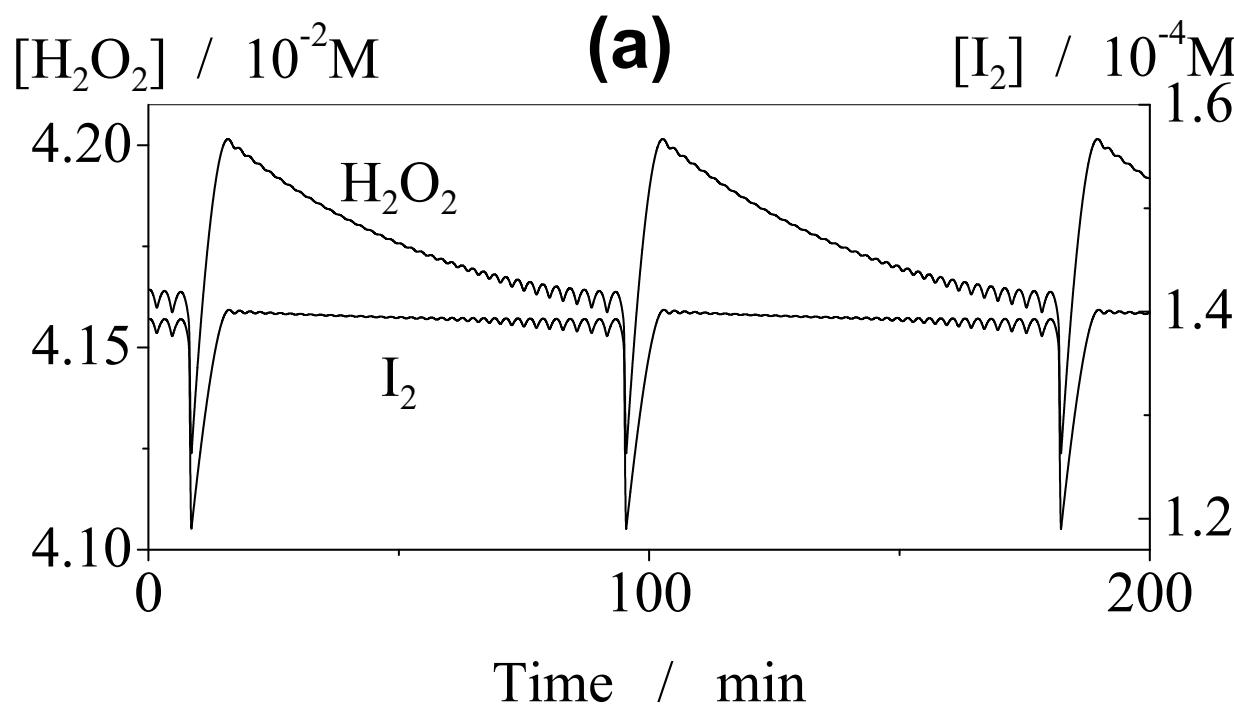
Numeričke simulacije



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

Eksperimentalna merenja su ograničena na nekoliko vrsta



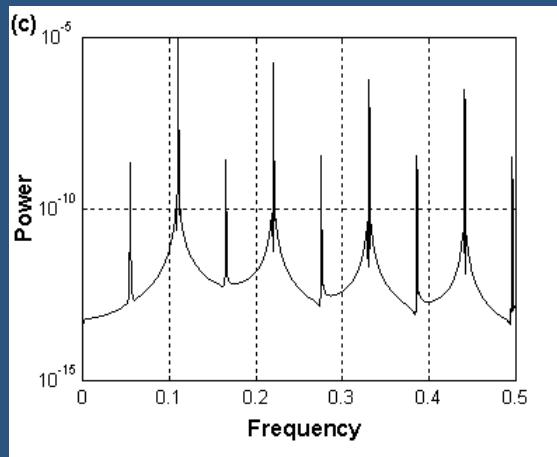
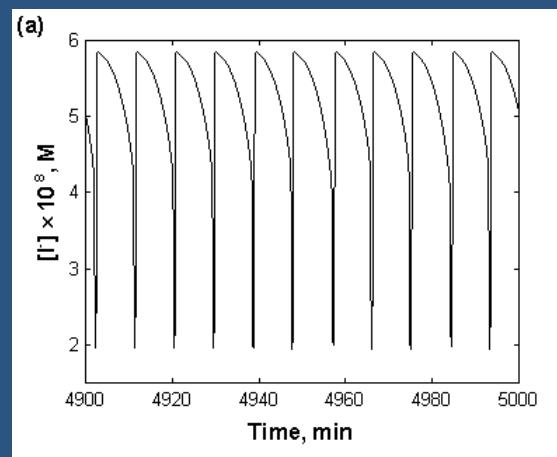
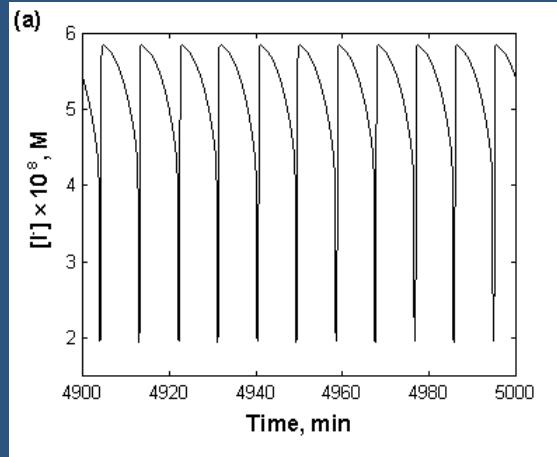


Za opisivanje stanja sistema u proizvoljnom trenutku neophodno je poznavanje koncentracija svih reaktanata i još većeg broja intermedijera

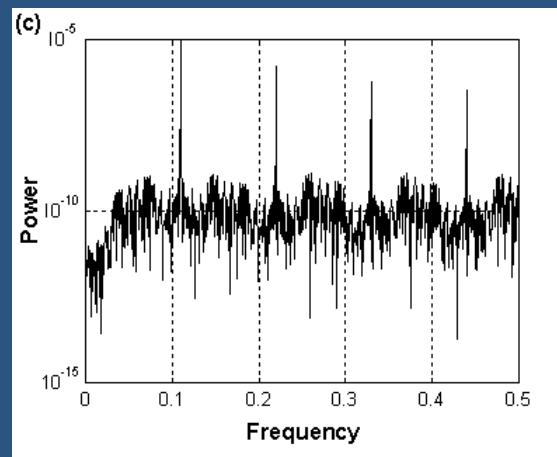
Spektri snage – metoda za analizu oscilatornih procesa

Spektar snage je kvadrat modula furijeove transformacije signala.

Prilikom udvajanja perioda dolazi do pojave subharmonika u spektru snage.



Slika 1



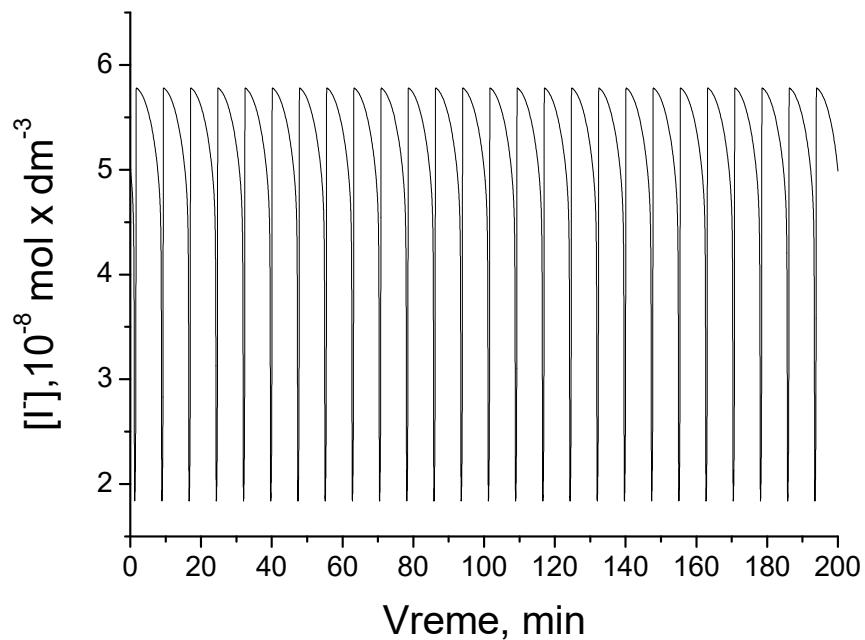
Slika 1:
Period-2 oscilacije
kada je
 $j_0 = 4.824 \times 10^{-3} \text{ min}^{-1}$;
(a) vremenska serija,
i
(c) spektar snage.

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

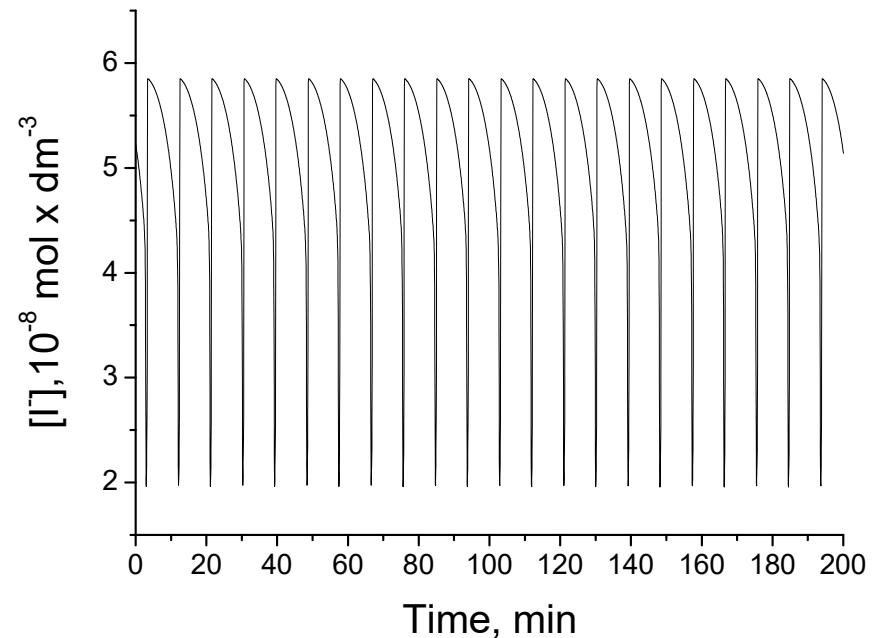
Guy Schmitz, Ljiljana Kolar-Anić,
Slobodan Anić, Tomislav Grozdić,
Vladana Vukojević
J. Phys. Chem. A,
110 (2006) 10361-10368.

Slika 2

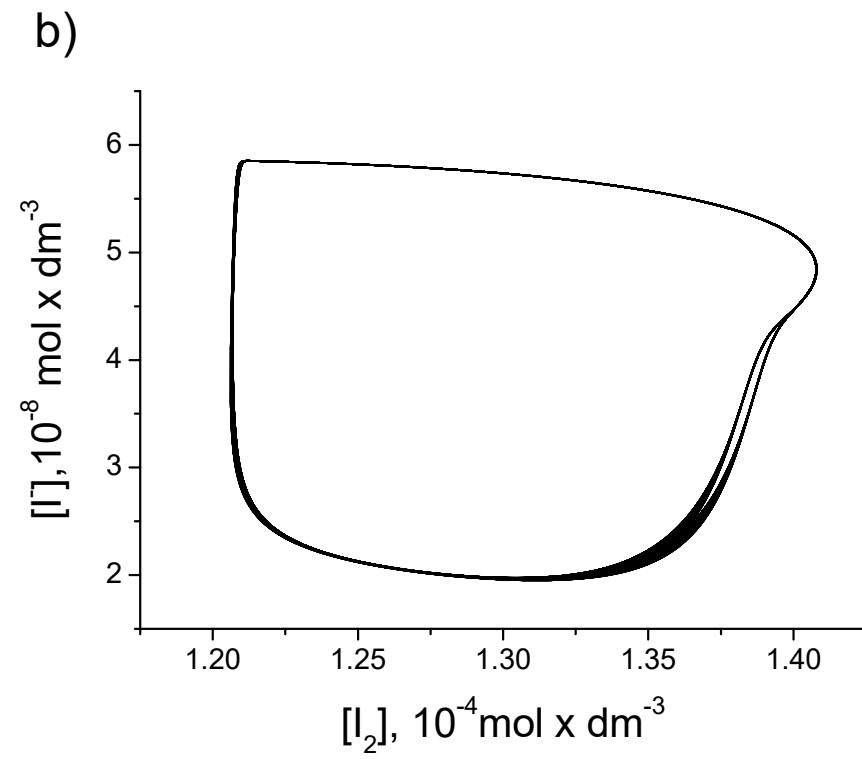
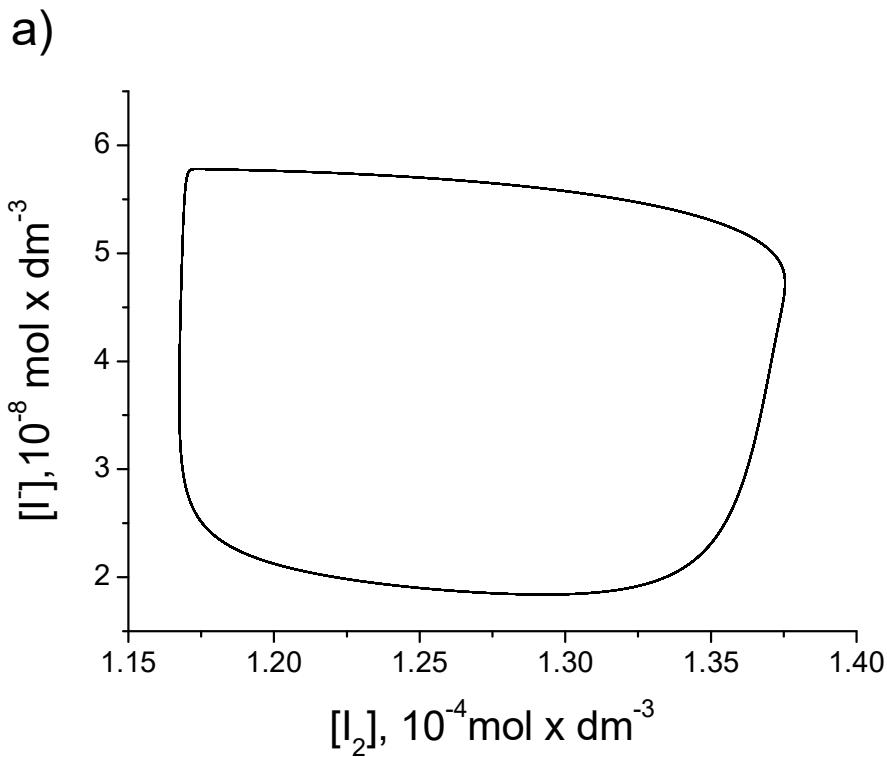
a)



b)



- a) Vremenska serija koja odgovara protoku $j_0=4.5 \times 10^{-3} \text{ min}^{-1}$ (1^0) i
b) vremenska serija koja odgovara protoku $j_0=4.824 \times 10^{-3} \text{ min}^{-1}$ (1^0)₂.



- a) Atraktor koji odgovara protoku $j_0=4.5 \times 10^{-3} \text{ min}^{-1}$ (1^0) i
b) Atraktor koji odgovara protoku $j_0=4.824 \times 10^{-3} \text{ min}^{-1}$ (1^0)₂.

Sadržaj II časa

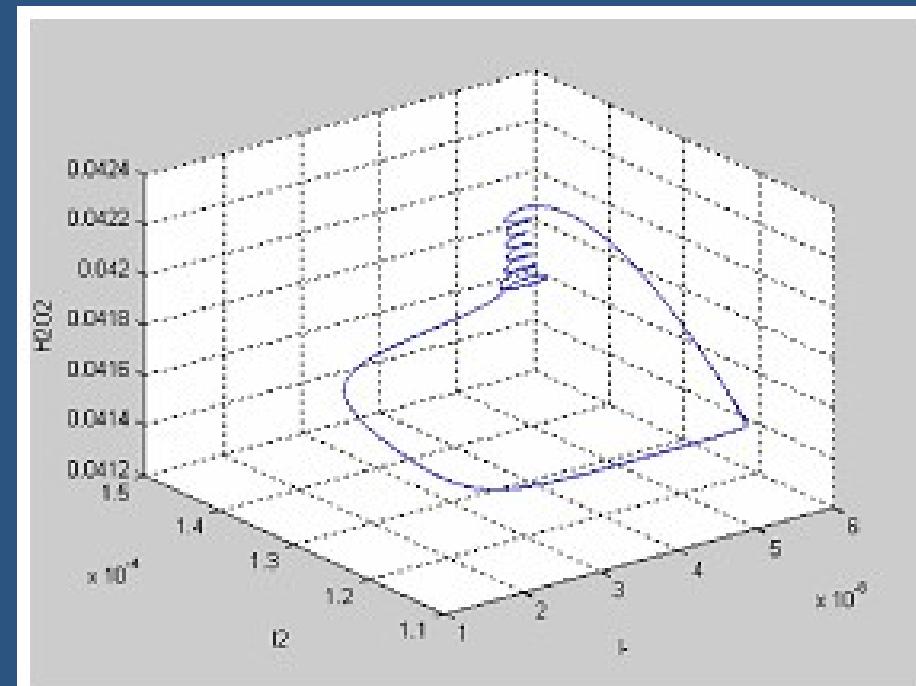
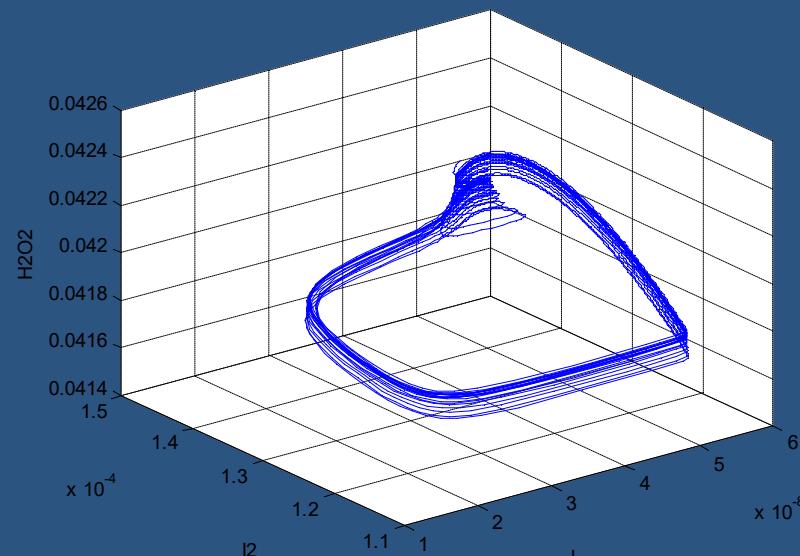
- Analiza vremenskih serija
 - **Analiza atraktora**
 - Bifurkaciona analiza
 - Interaktivne metode analize

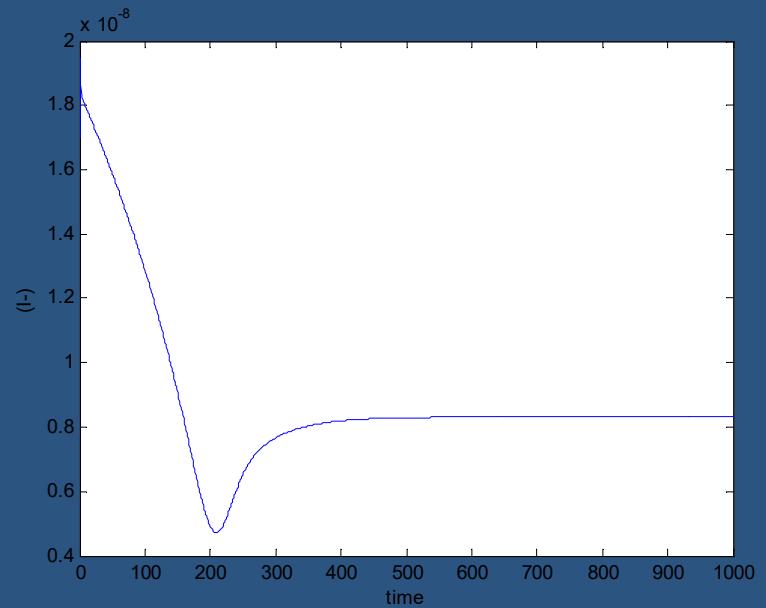
Fazni prostor i atraktor

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

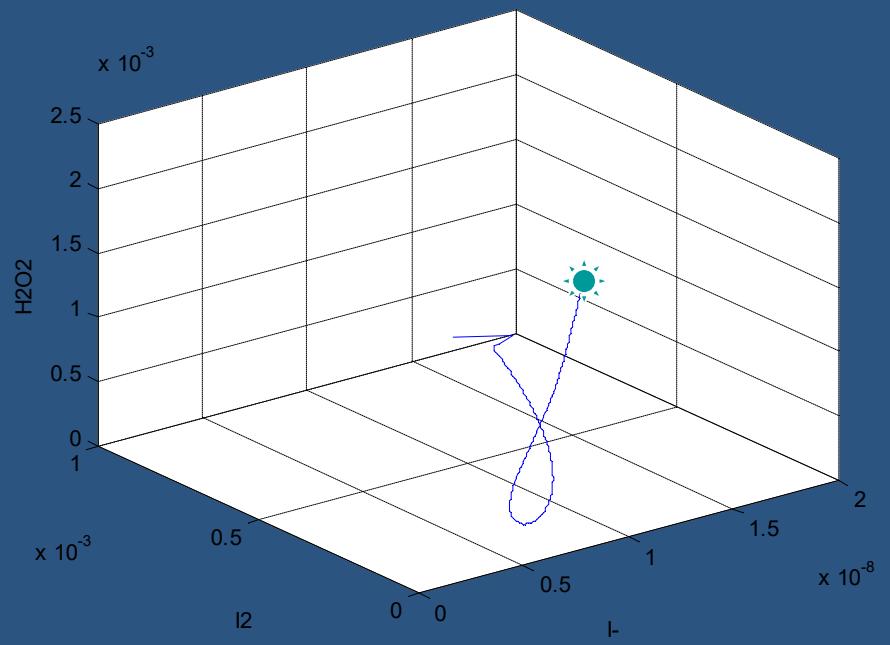
Haotičnoj dinamici odgovara otvorena putanja po ograničenom delu faznog prostora

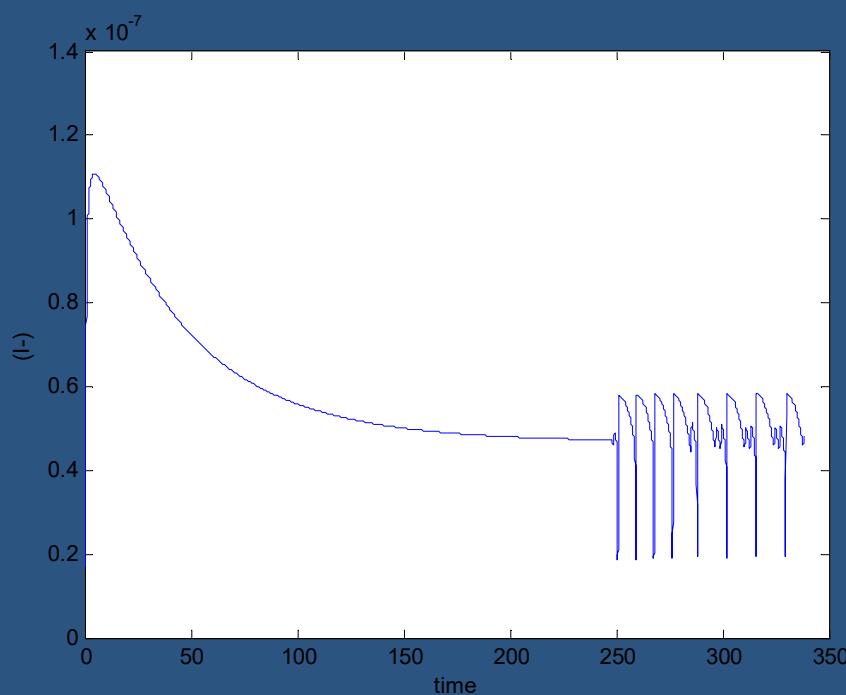
Atraktor je trajektorija dinamičkog sistema u faznom prostoru posle prolaska tranzijentnog perioda.



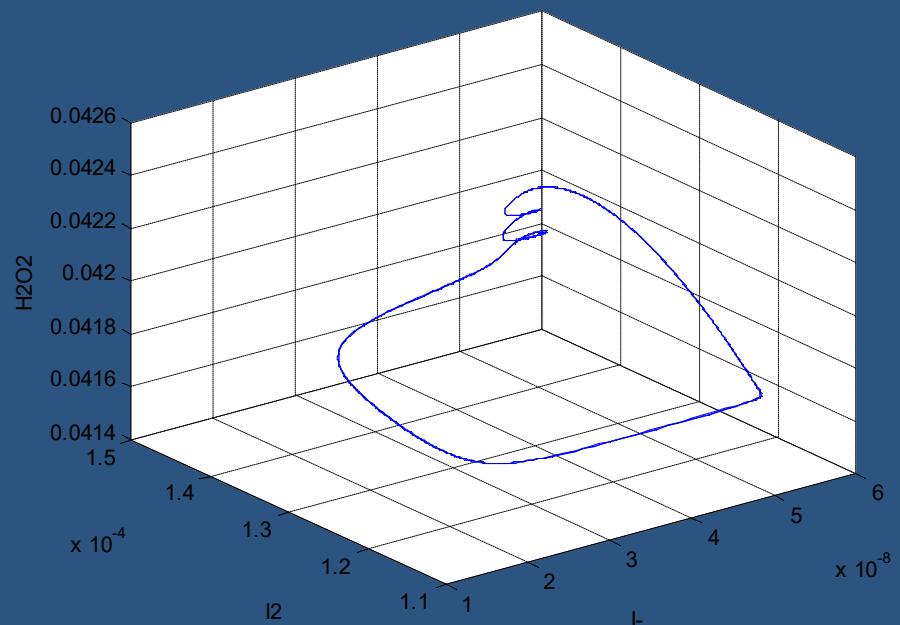
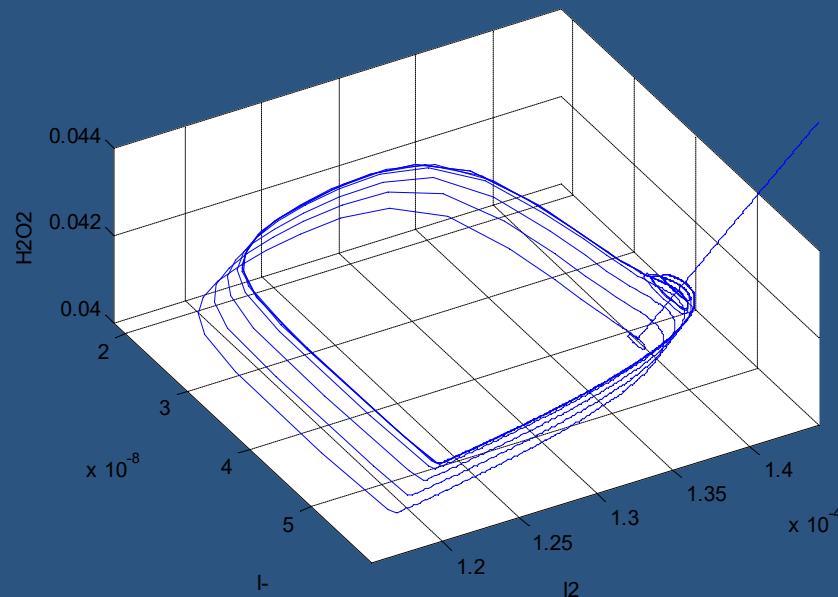


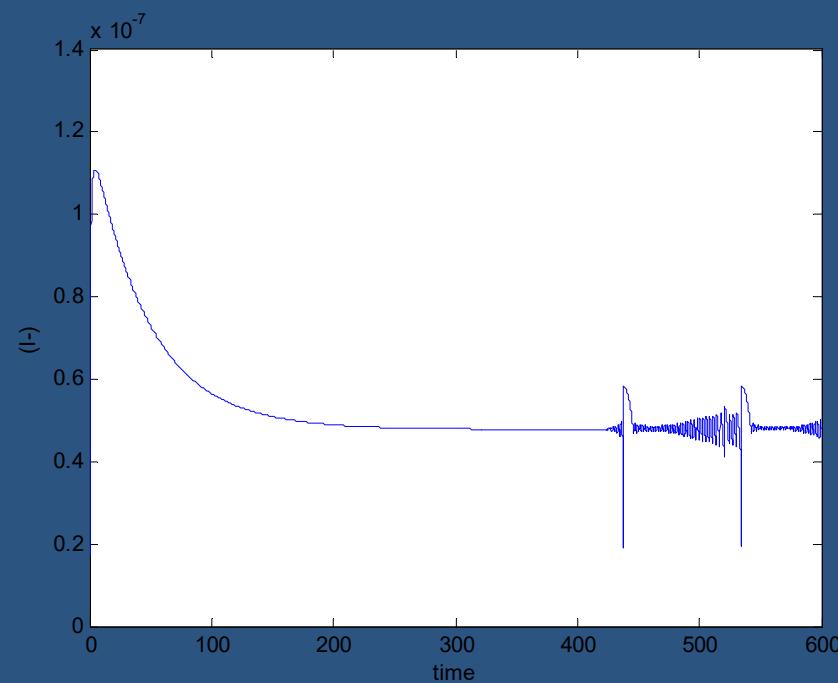
Slučaj 1 (stabilnost): Atraktor je
STACIONARNO STANJE



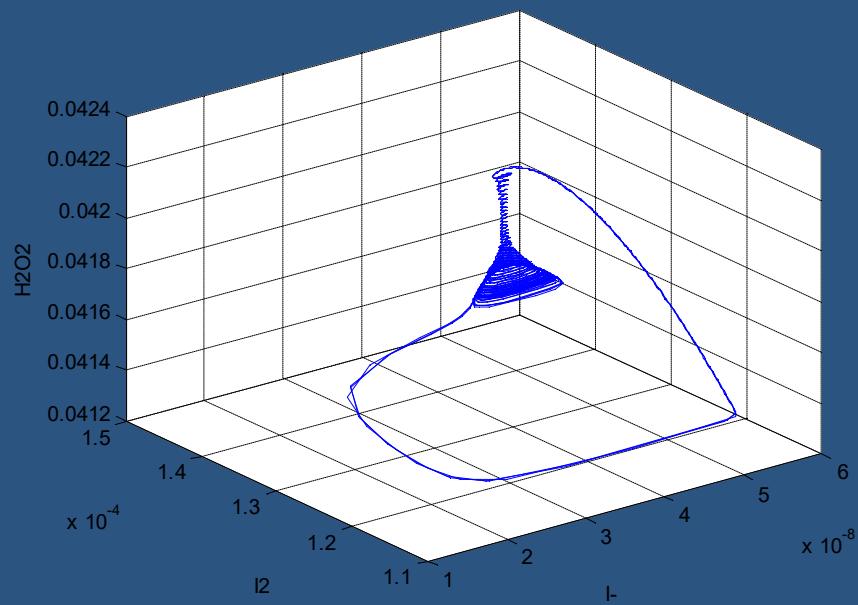
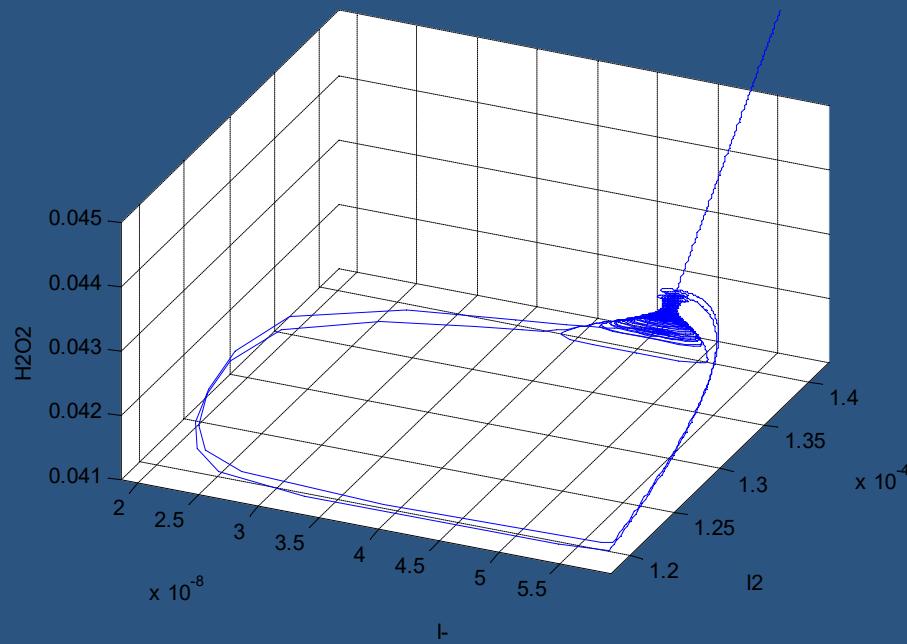
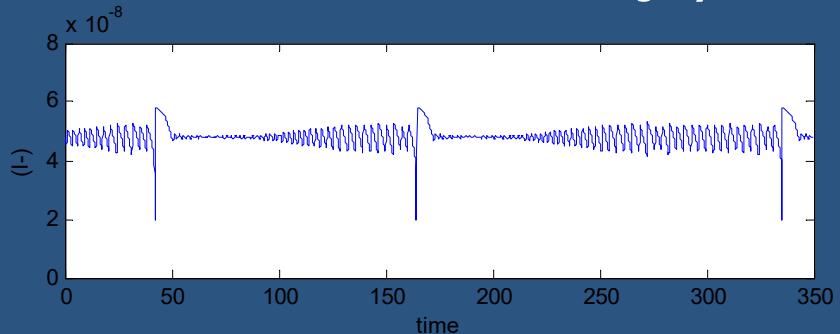


Slučaj 2: Atraktor je GRANIČNI KRUG



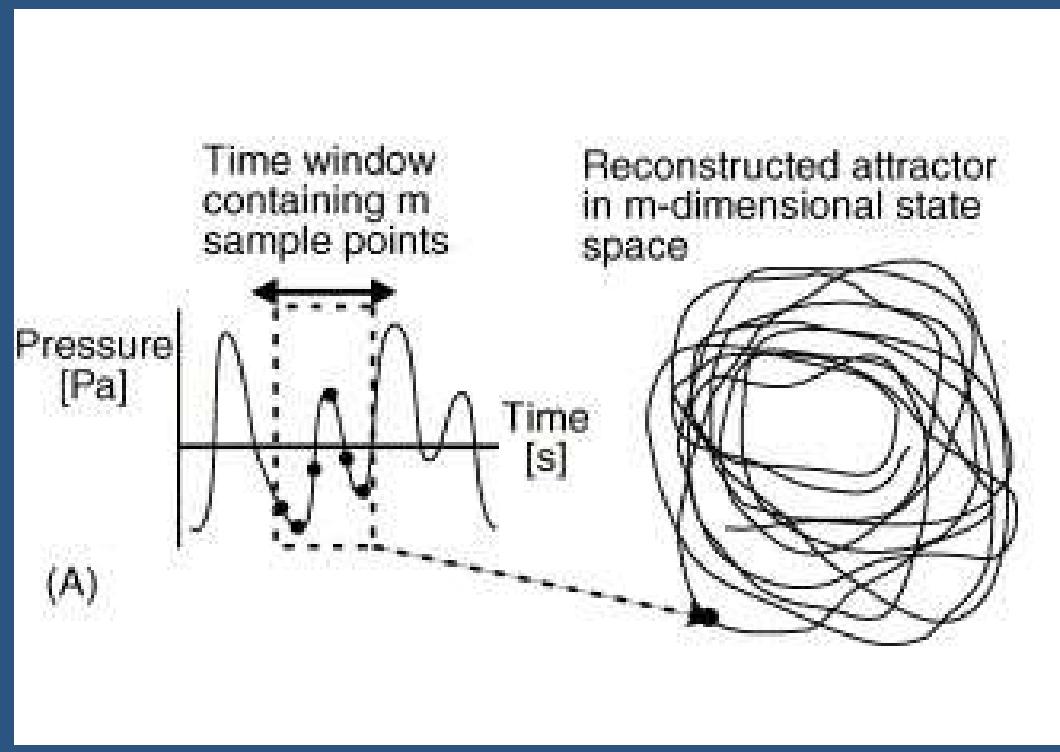


Slučaj 3 (haos): Atraktor je
ČUDNI ATRAKTOR
(fraktal – otvorena linija)

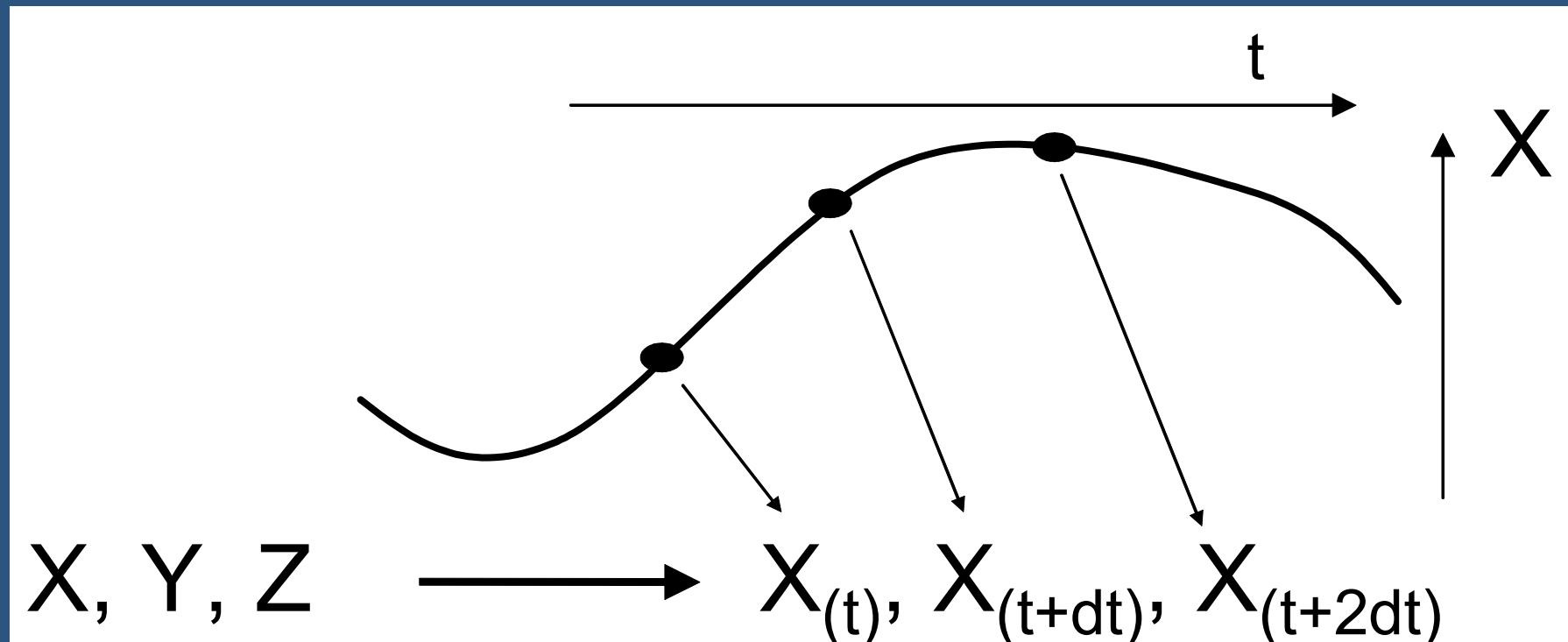


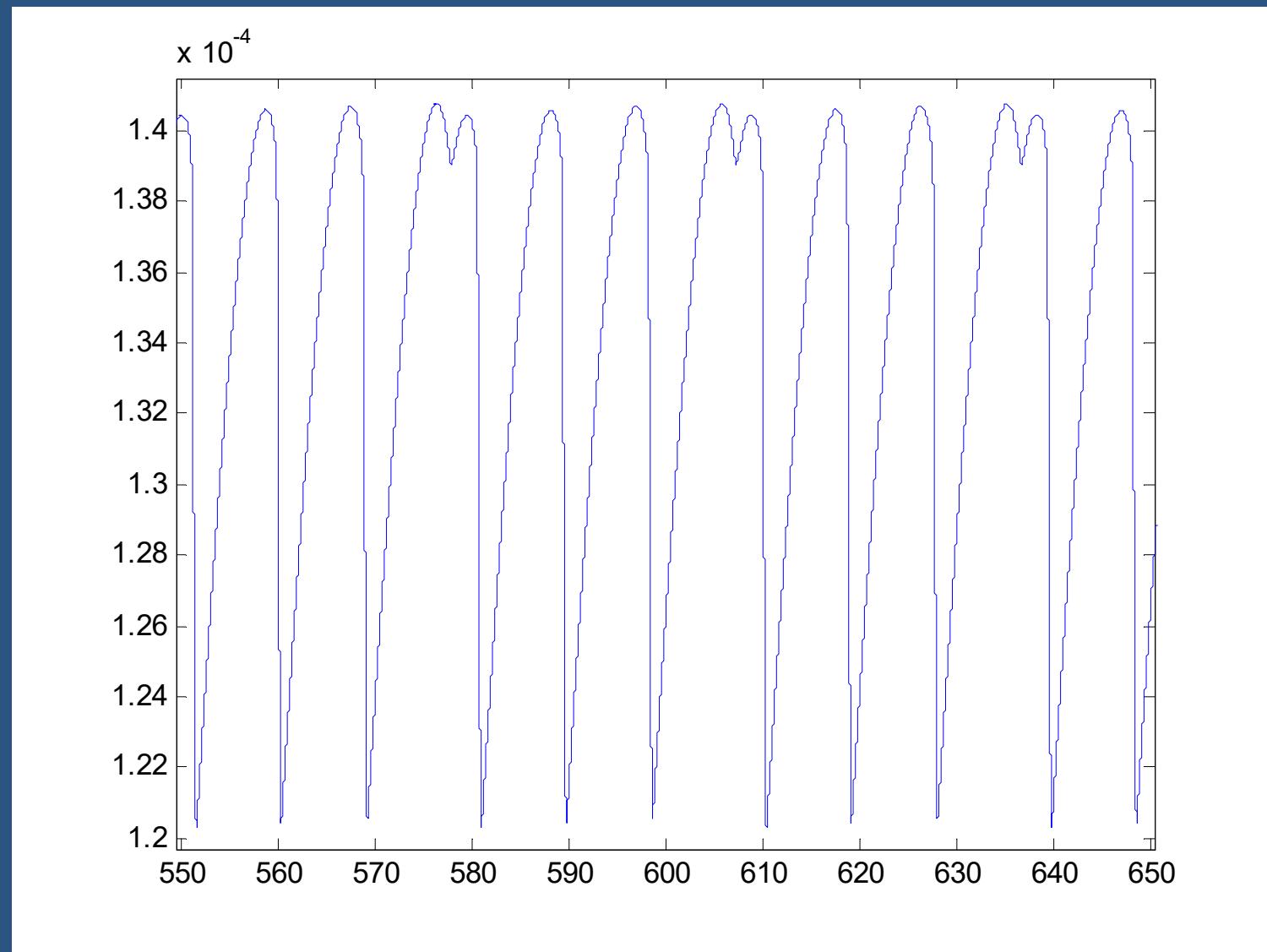
Rekonstrukcija atraktora

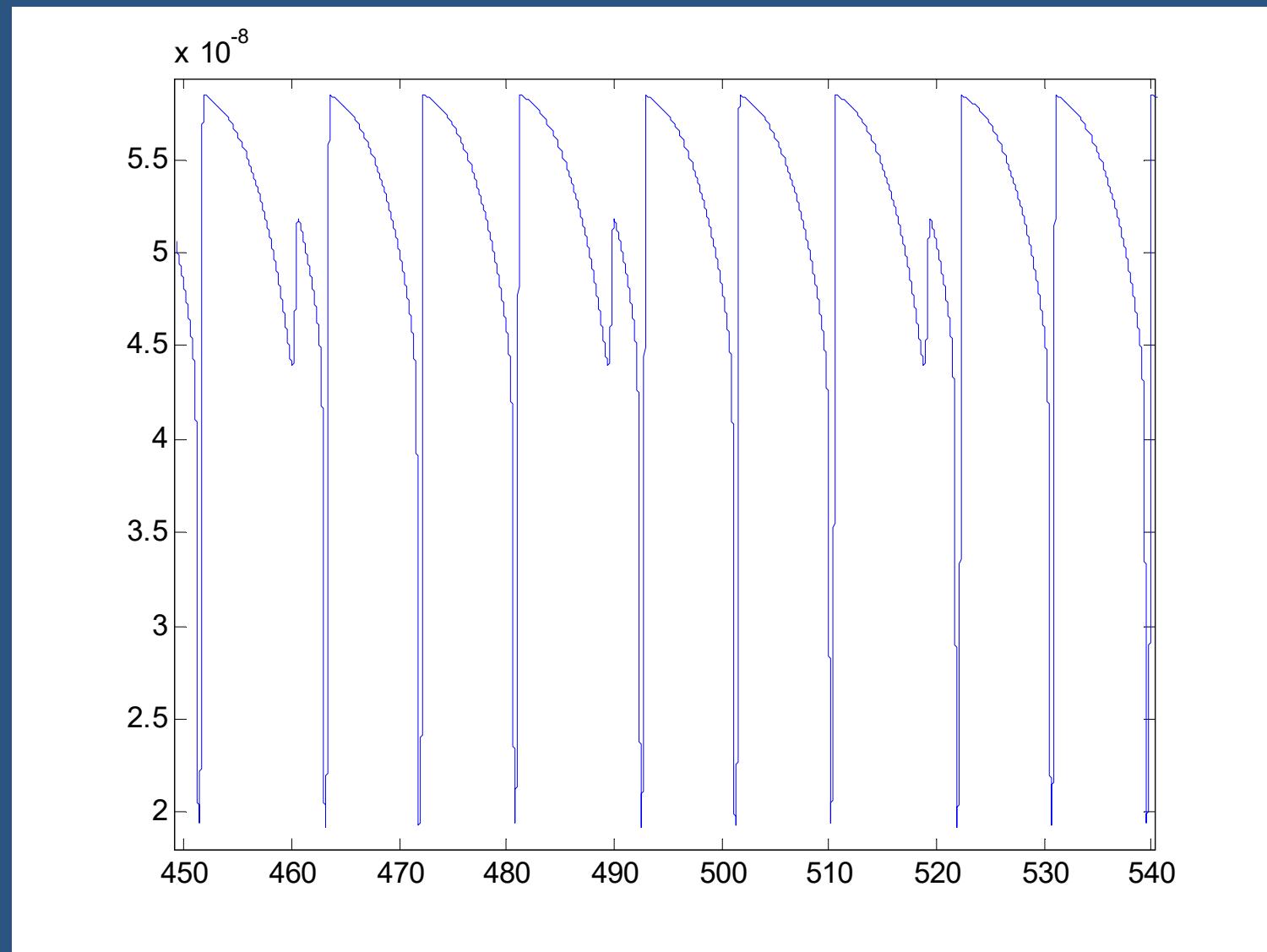
Takens je dokazao da umesto $2n+1$ generičkih signala, za prekrivanje n -dimenzionalnog atraktora može biti dovoljna konstrukcija sa vremenskim kašnjenjem $[y(t), y(t - \tau), y(t - 2\tau), \dots, y(t - 2n\tau)]$ izvedena iz samo jednog generičkog signala.

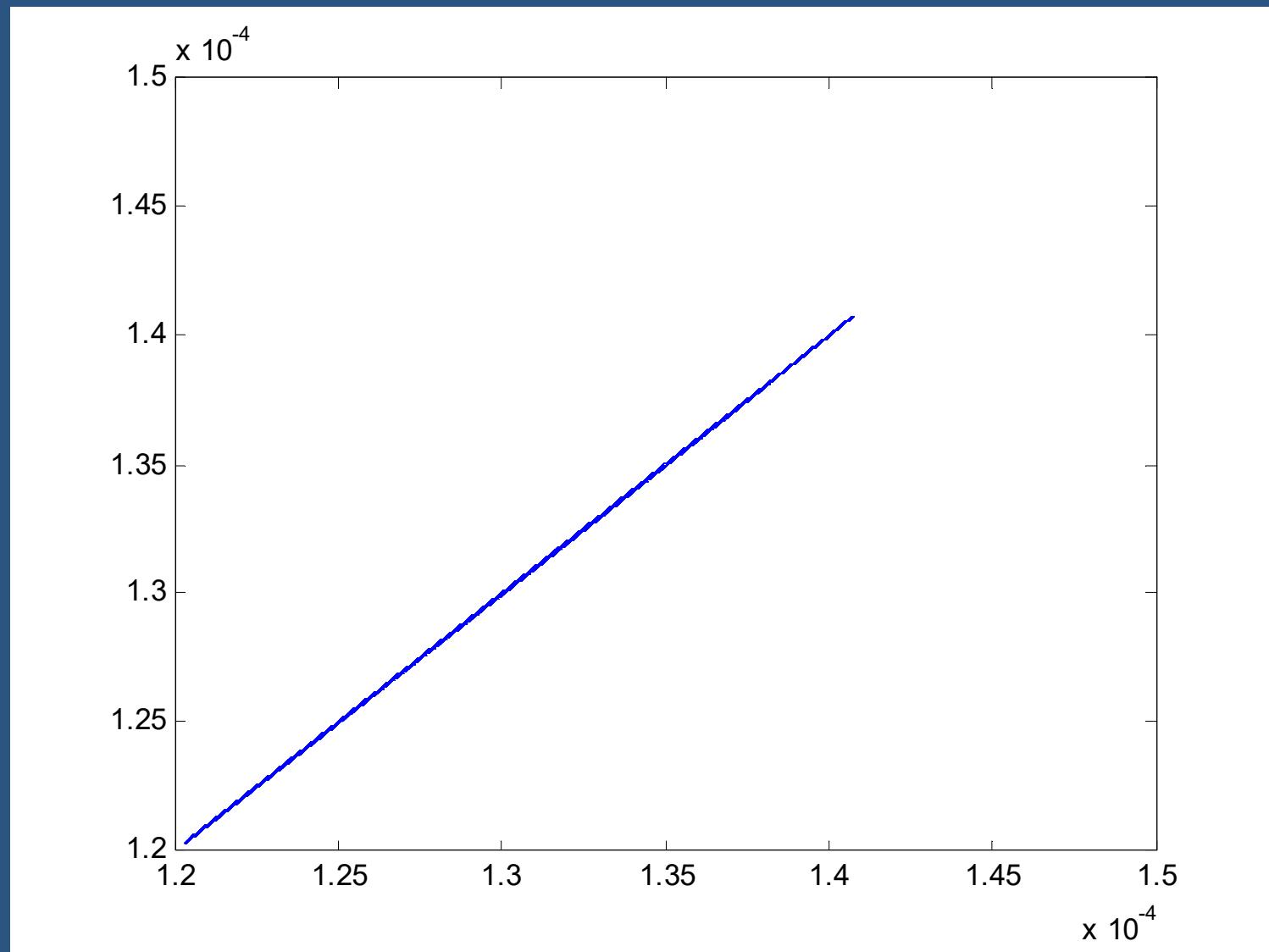


Takensov postupak

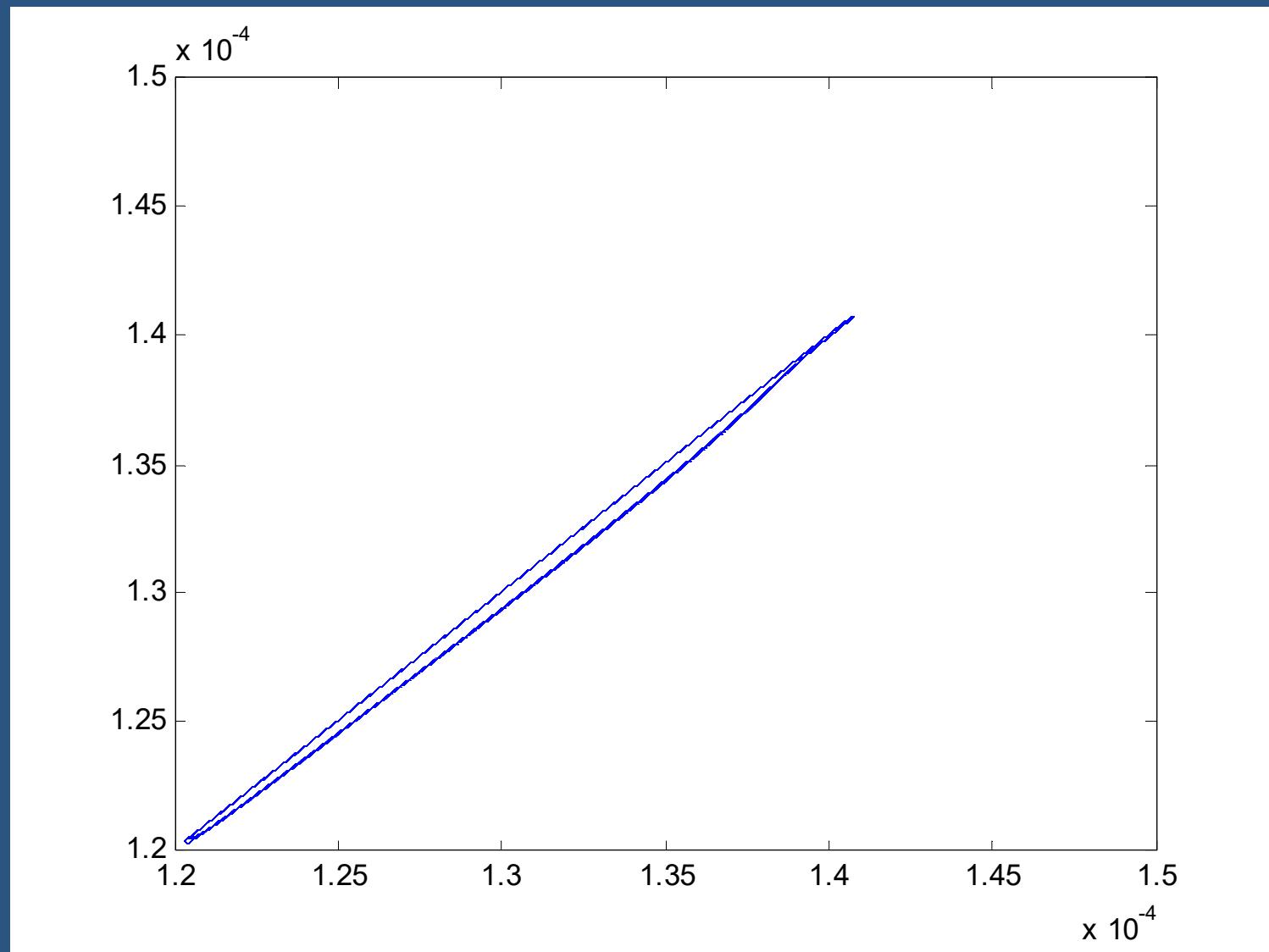




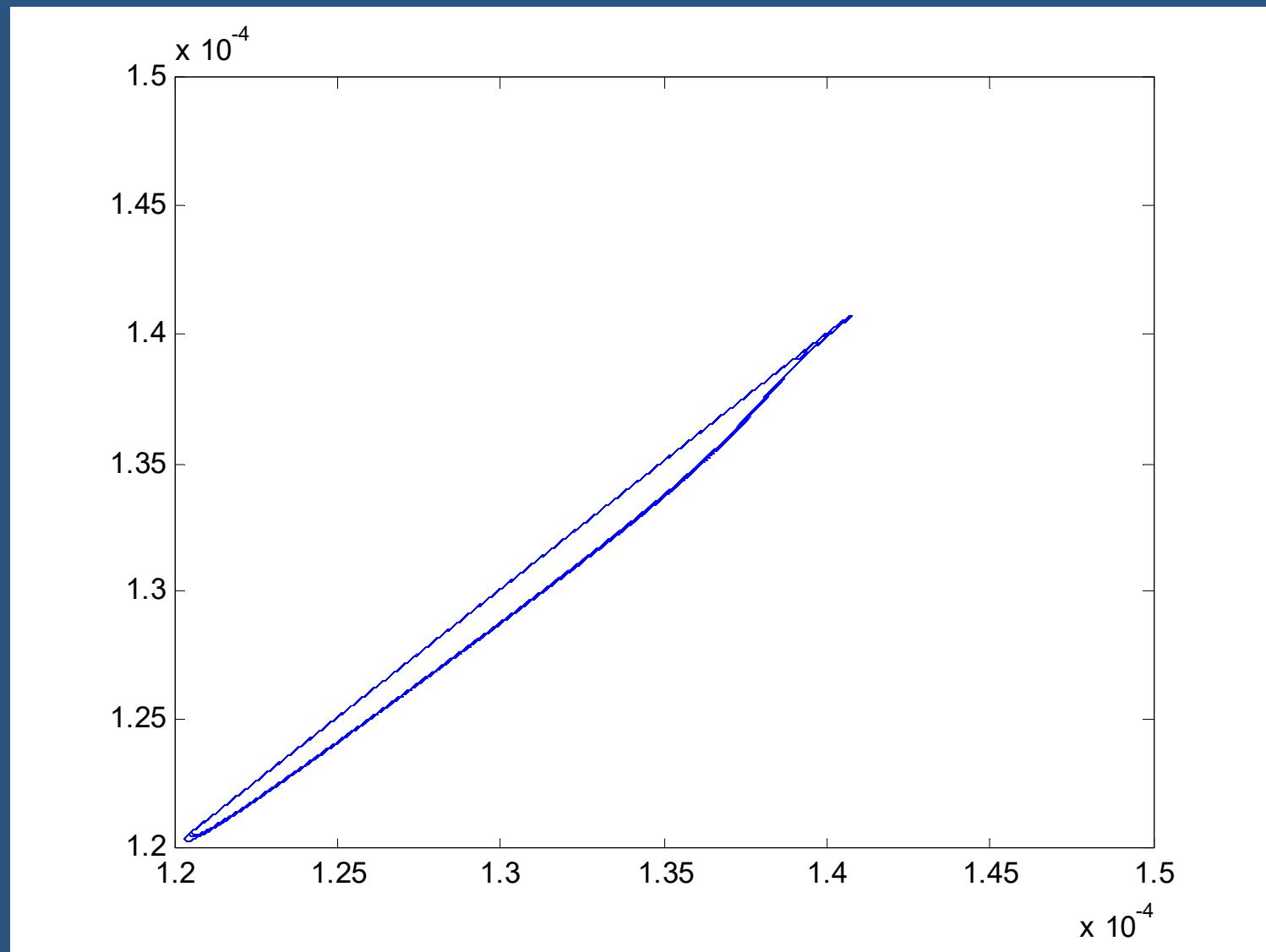




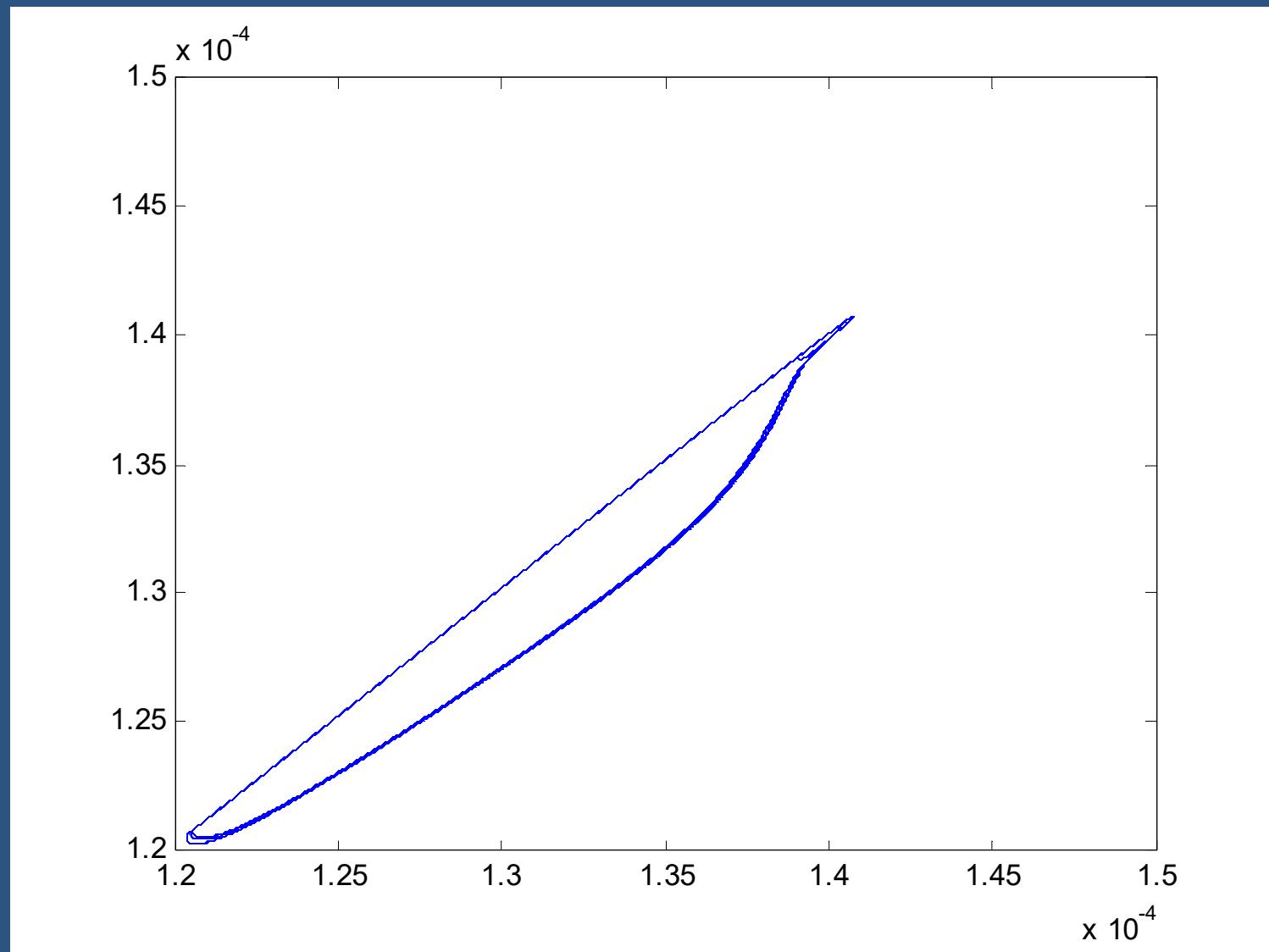
$\tau = 1$



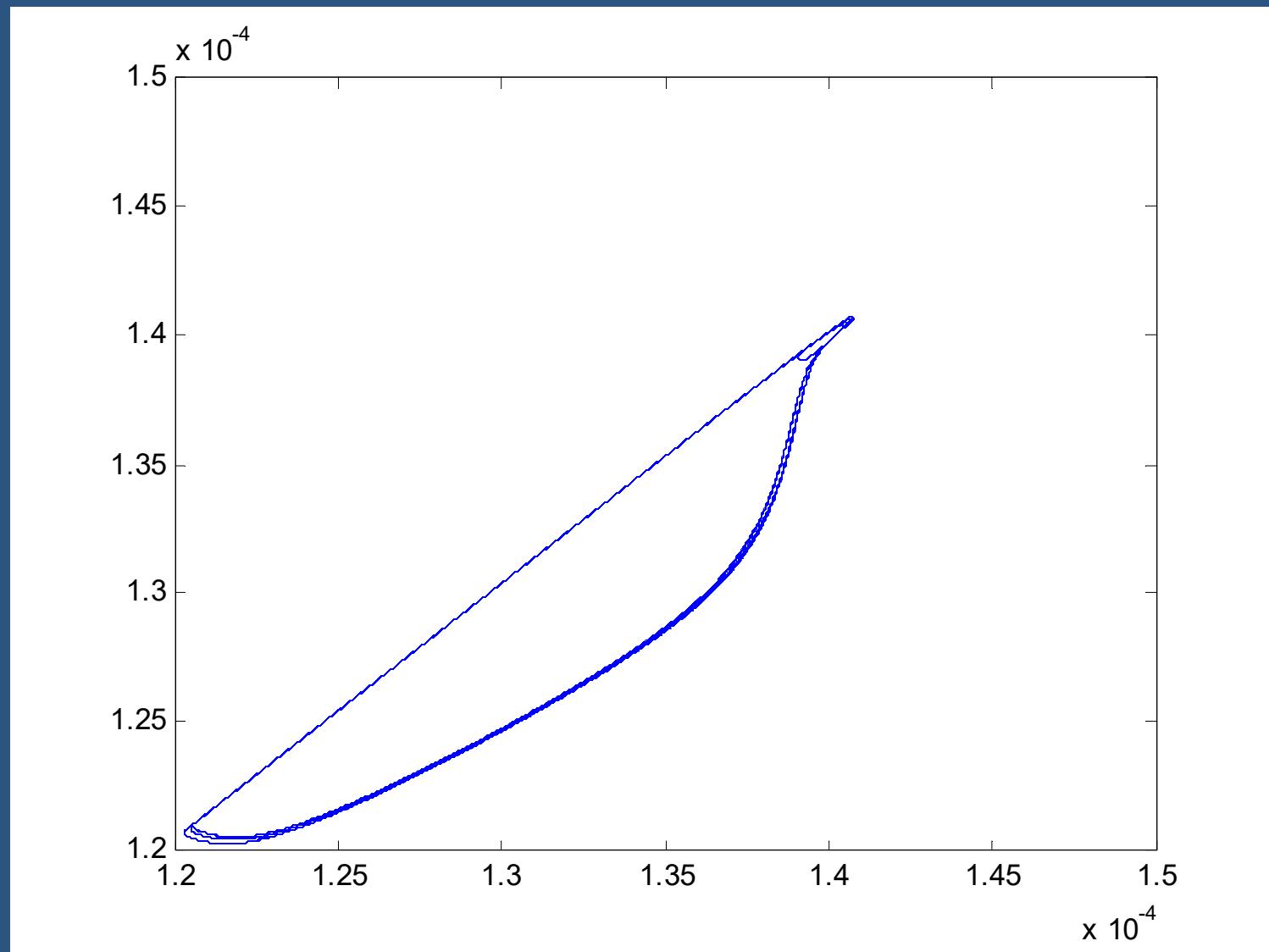
$\tau = 10$



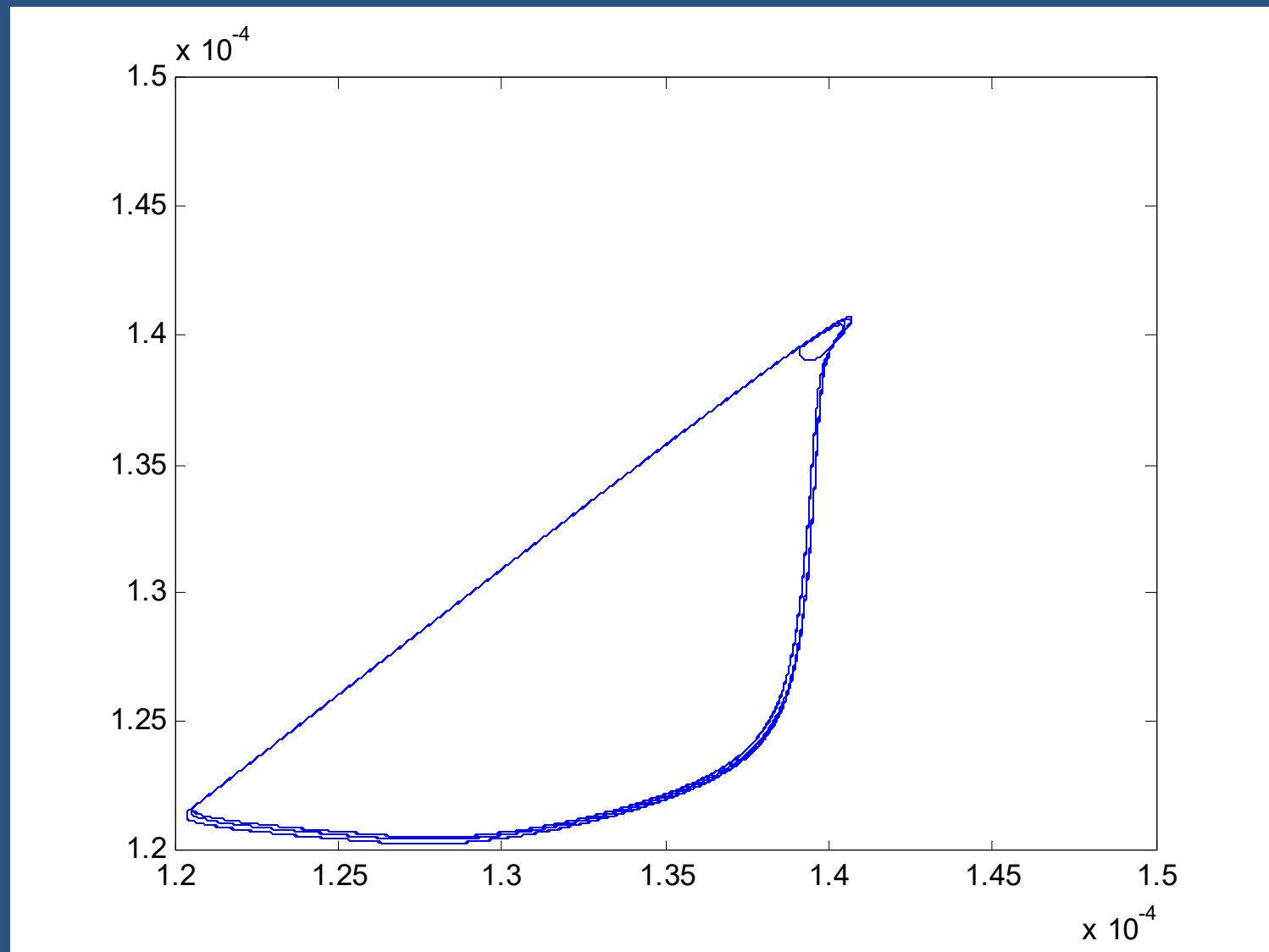
$\tau = 20$



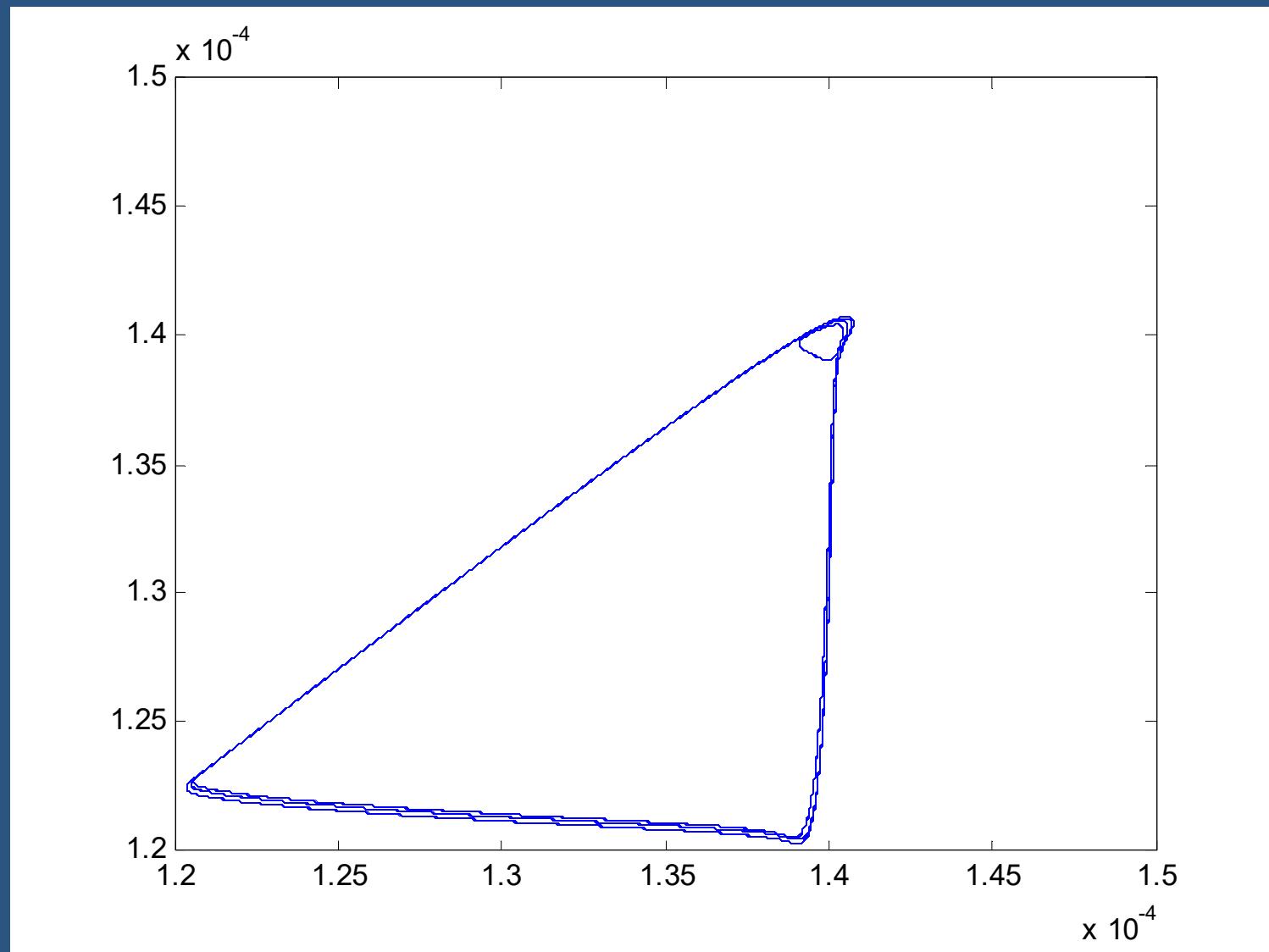
$\tau = 50$



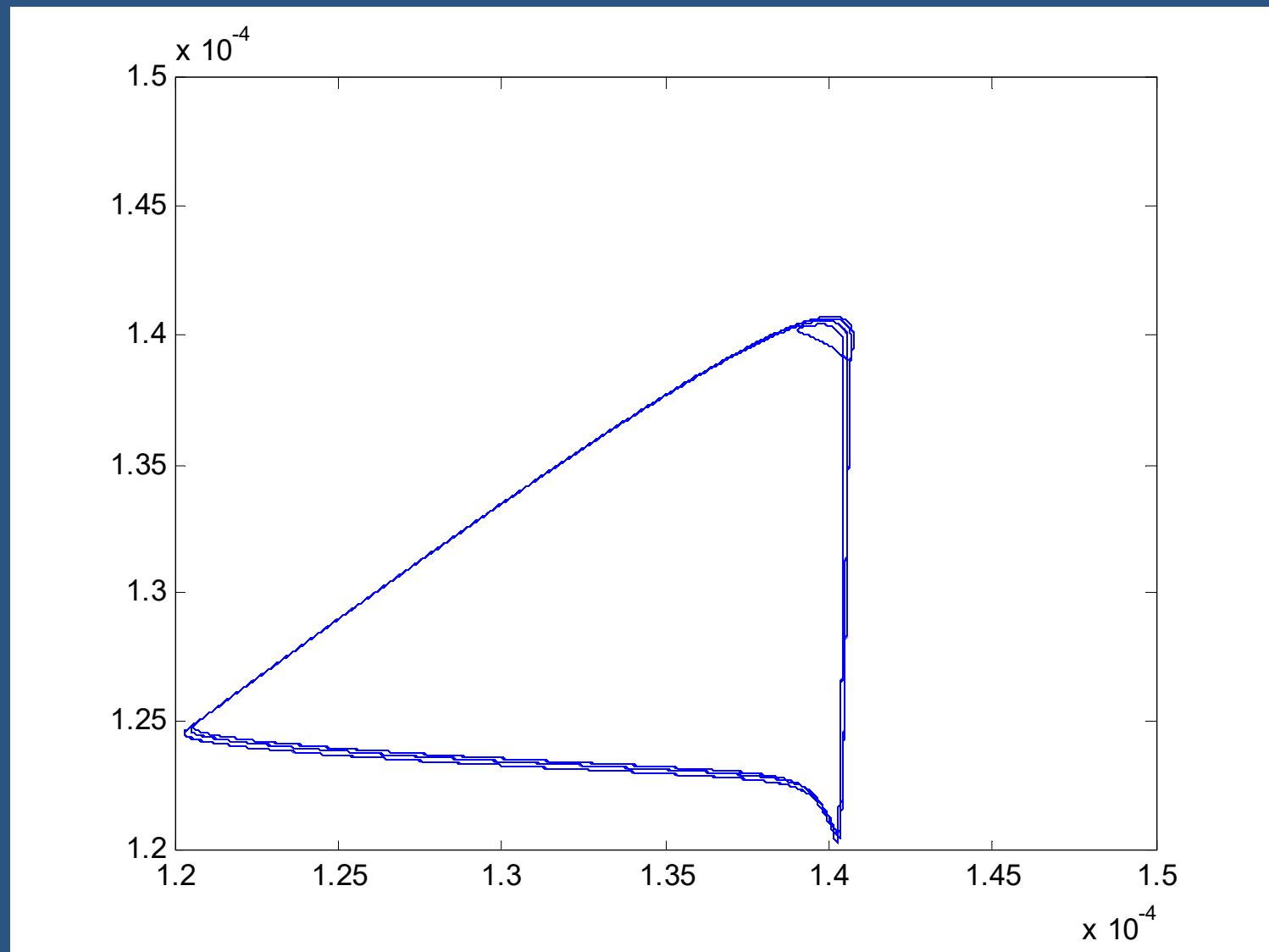
$\tau = 100$



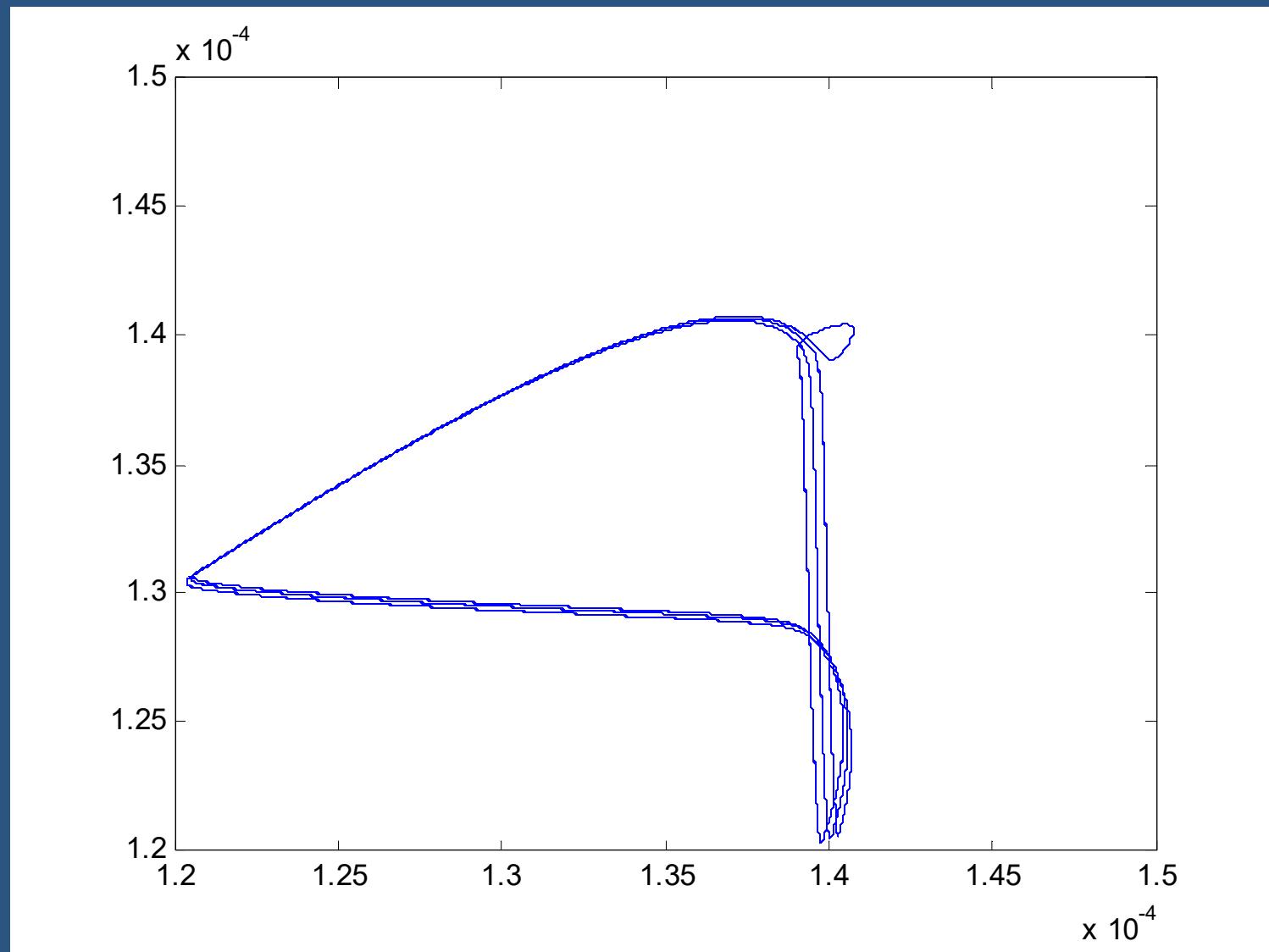
$\tau = 250$



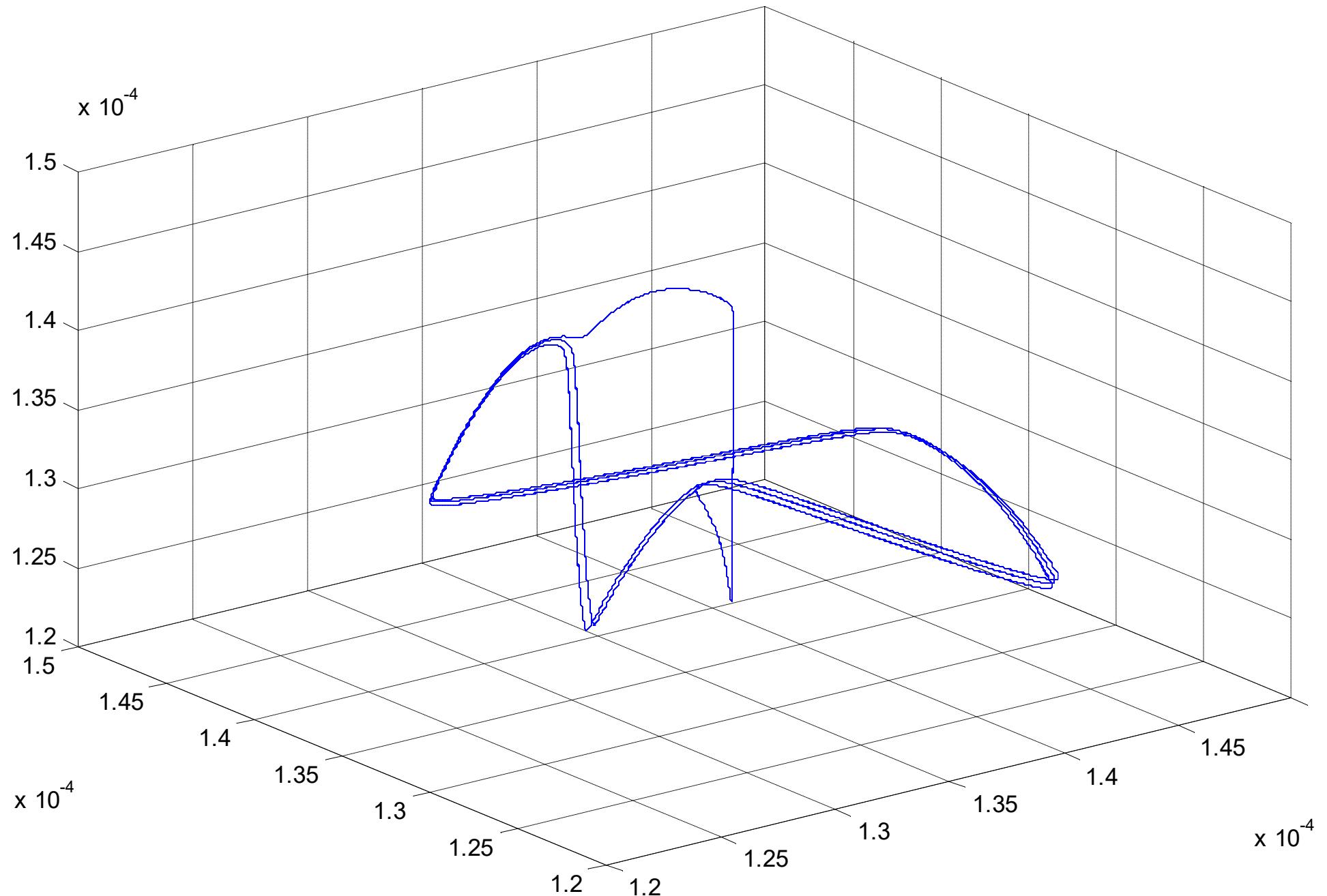
$\tau = 500$



$\tau = 1000$

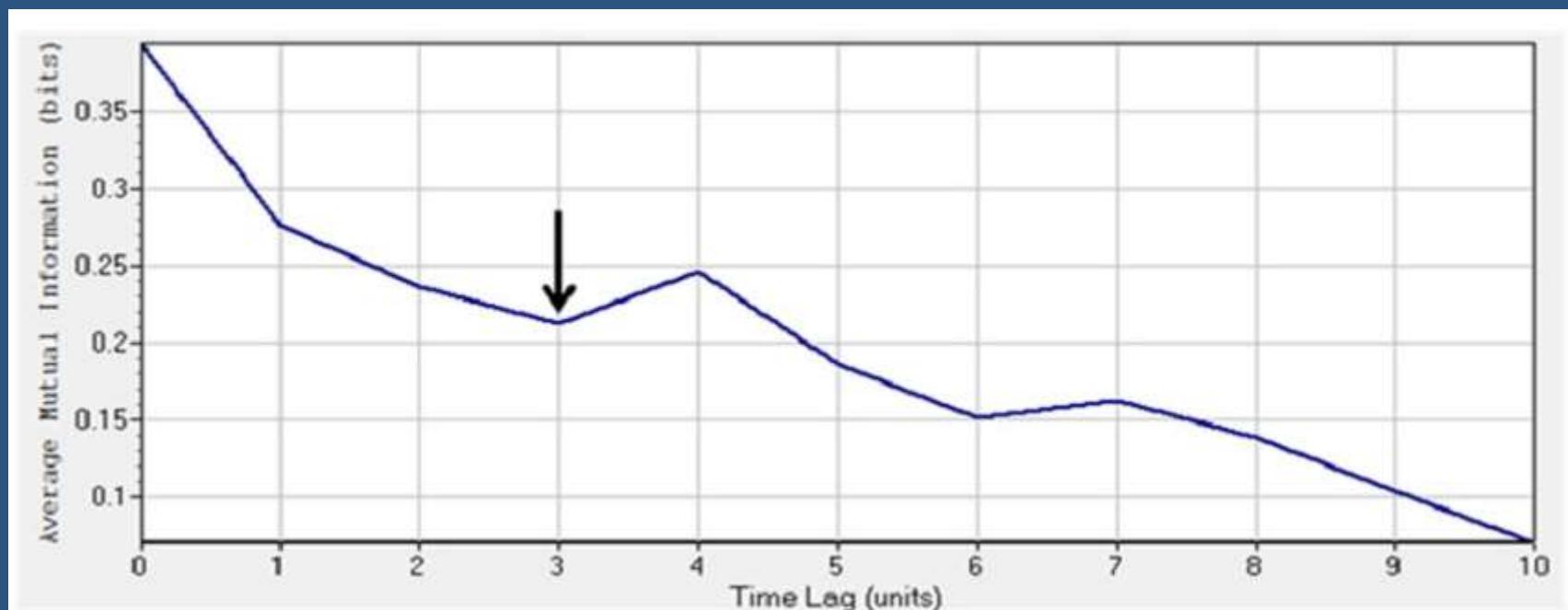


$\tau = 2500$



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

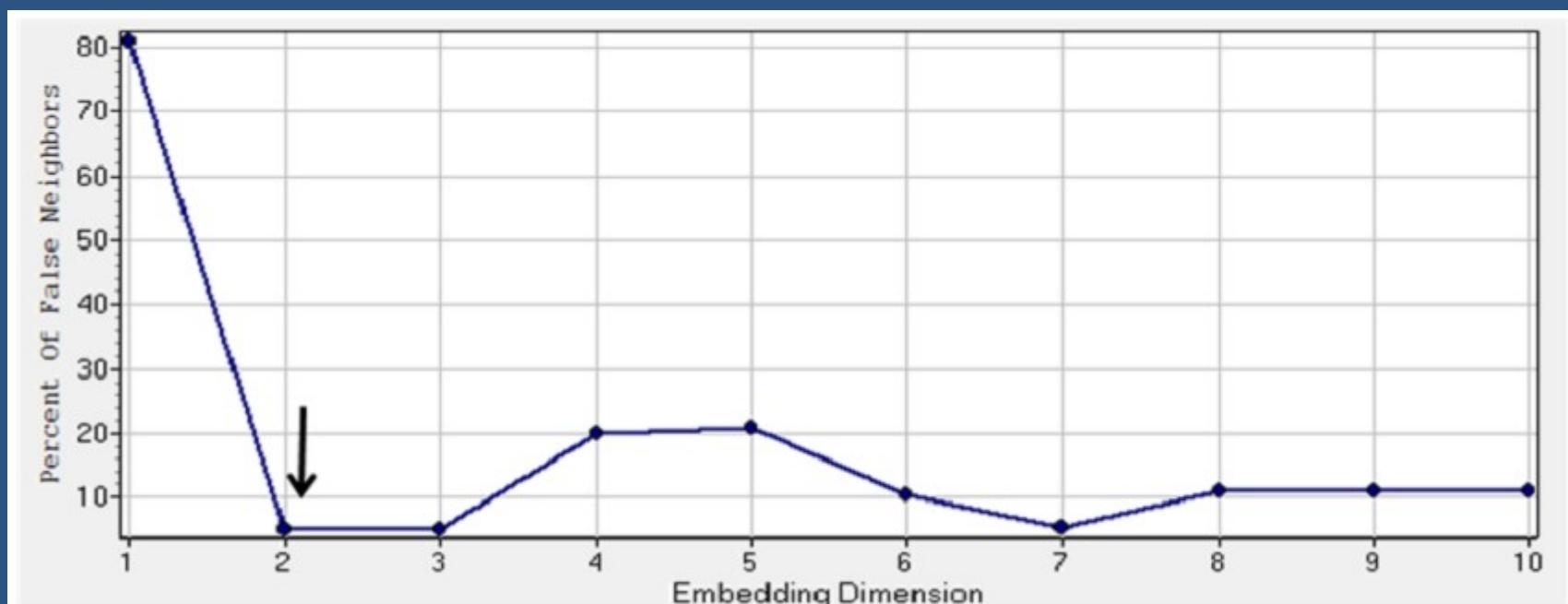
$$I(X; Y) = \sum_{y \in Y} \sum_{x \in X} p(x, y) \log \left(\frac{p(x, y)}{p(x) p(y)} \right),$$



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.

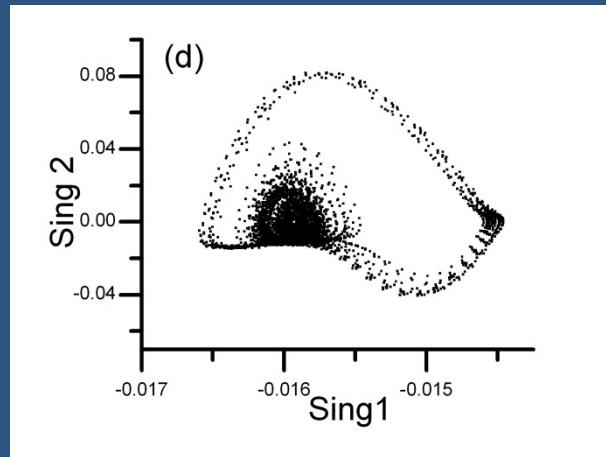
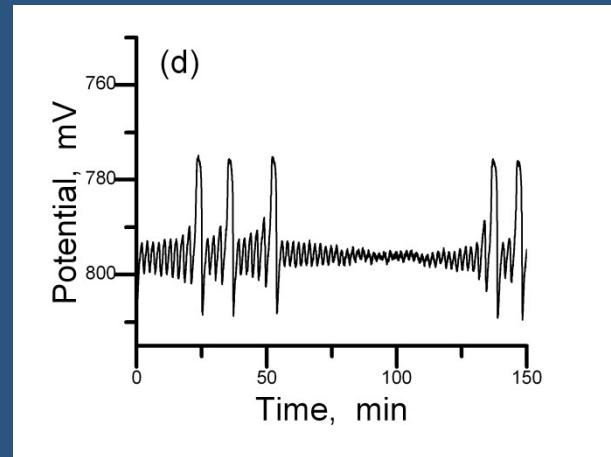
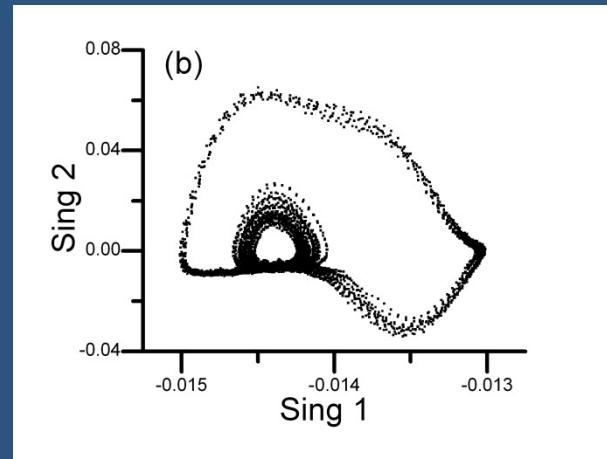
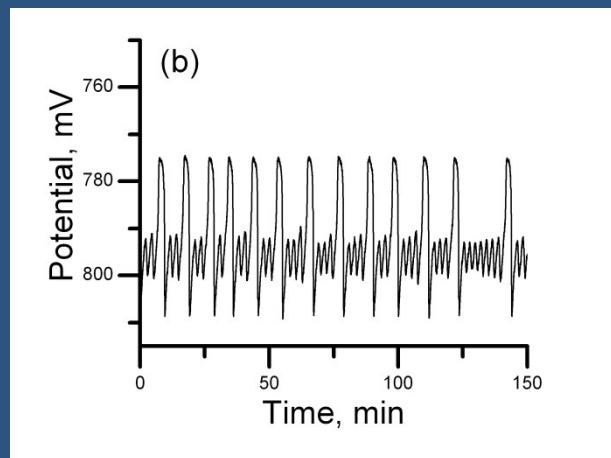
Singular value decomposition (SVD)

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

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

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

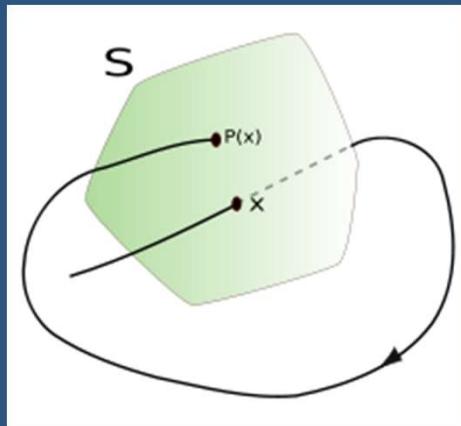


A. Z. Ivanović, Ž. D. Čupić, M. M. Janković Lj. Z. Kolar-Anić and S. R. Anić, The chaotic sequences in the Bray–Liebhafsky reaction in an open Reactor, *Phys. Chem. Chem. Phys.*, 2008, 10, 5848–5858

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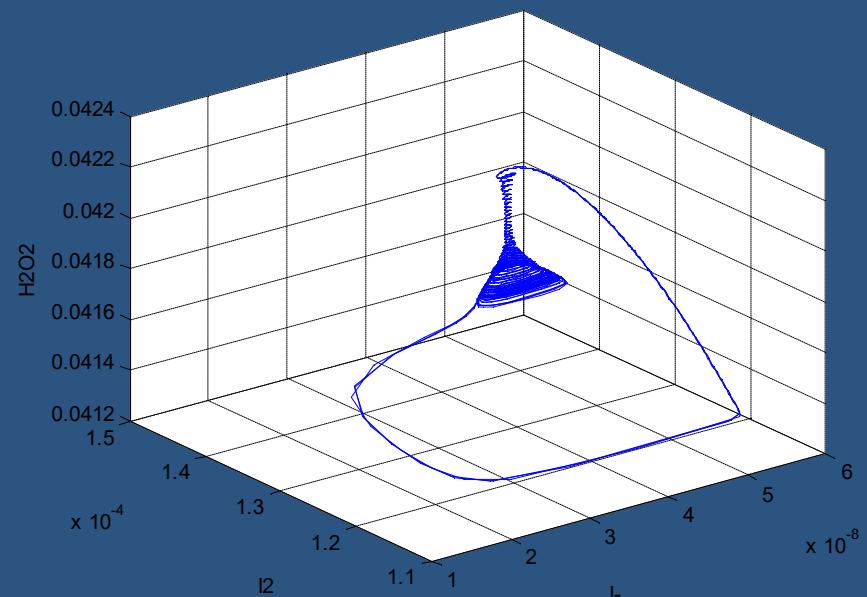
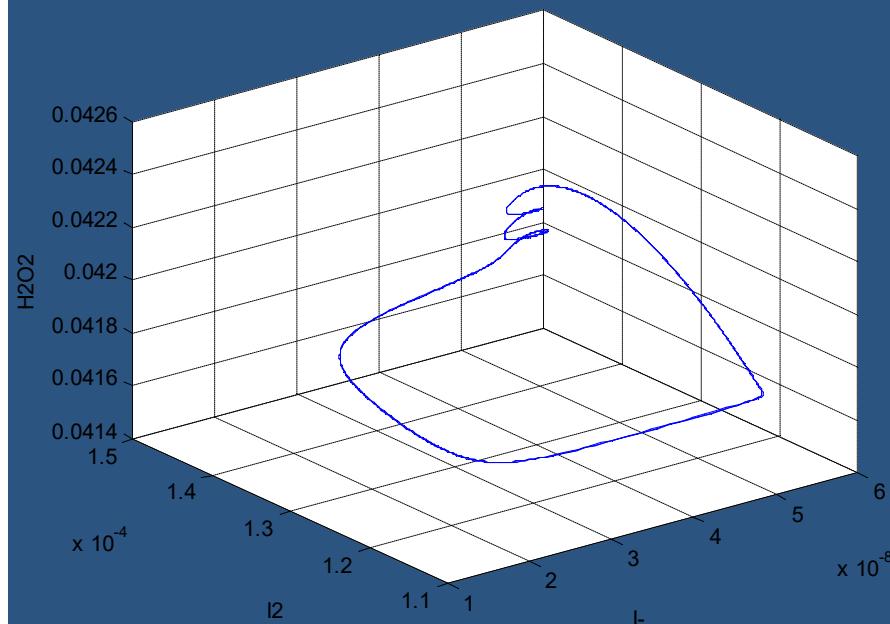
Poenkareovi preseci



Dimenzionalnost dinamičkog sistema se smanjuje i
Kontinualni dinamički sistem se diskretizuje

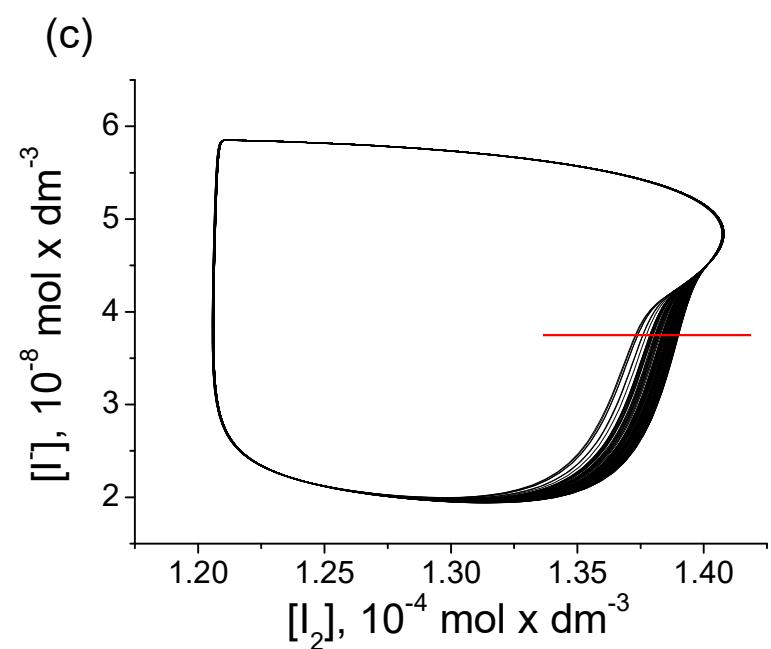
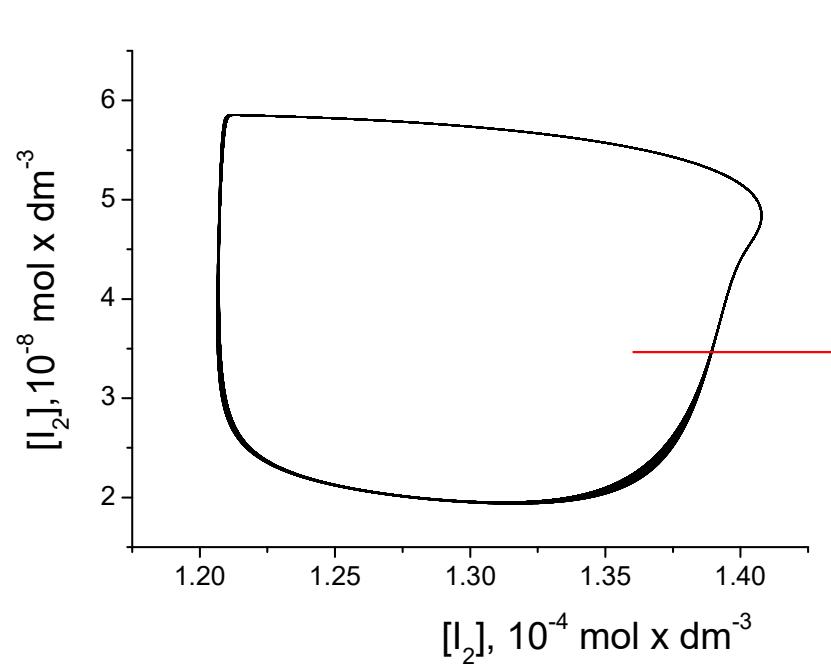
Periodični sistemi imaju diskretan mali broj tačaka u Poenkareovom preseku

Haotični sistemi imaju “neograničen broj” tačaka u Poenkareovom preseku

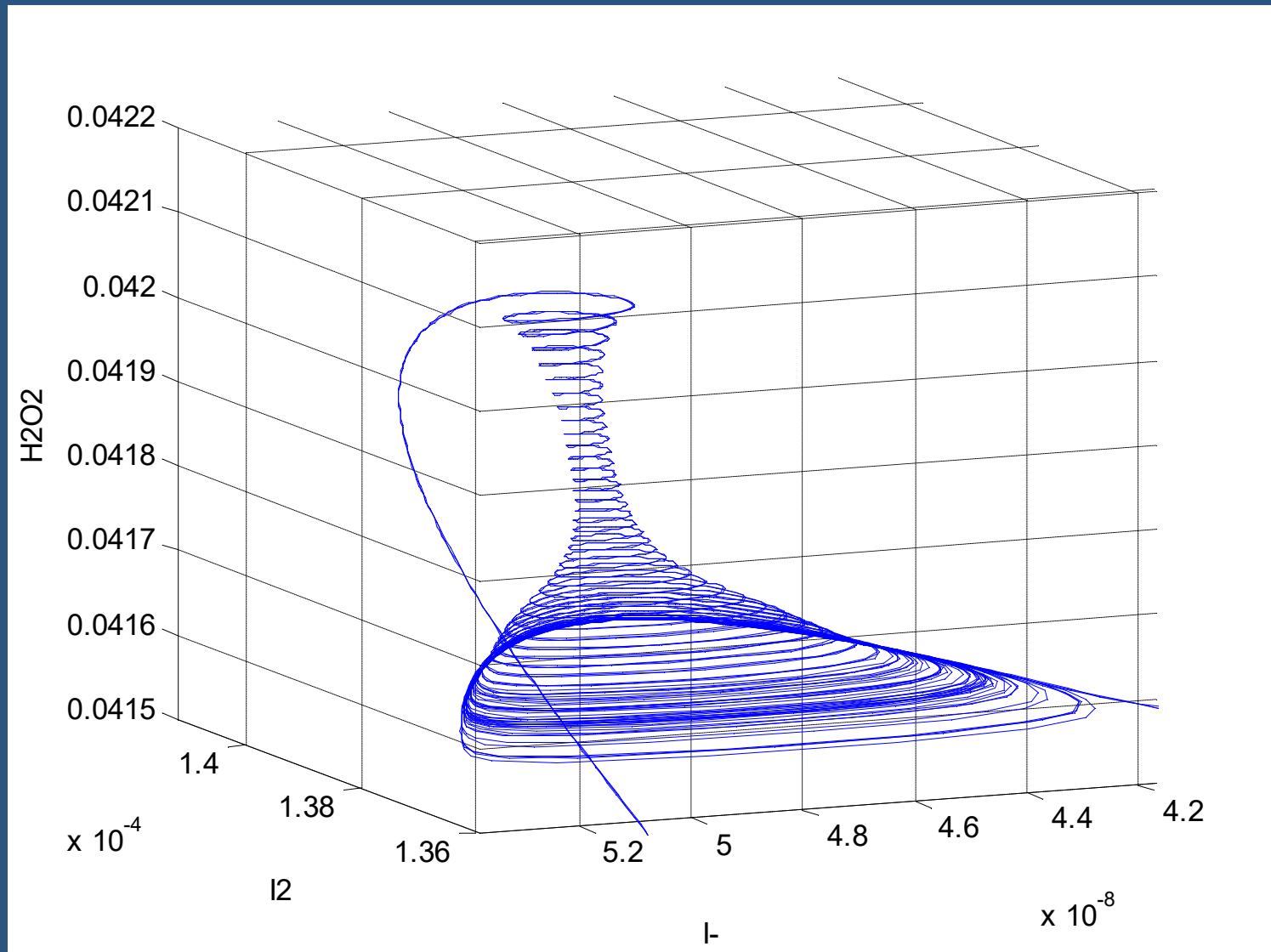


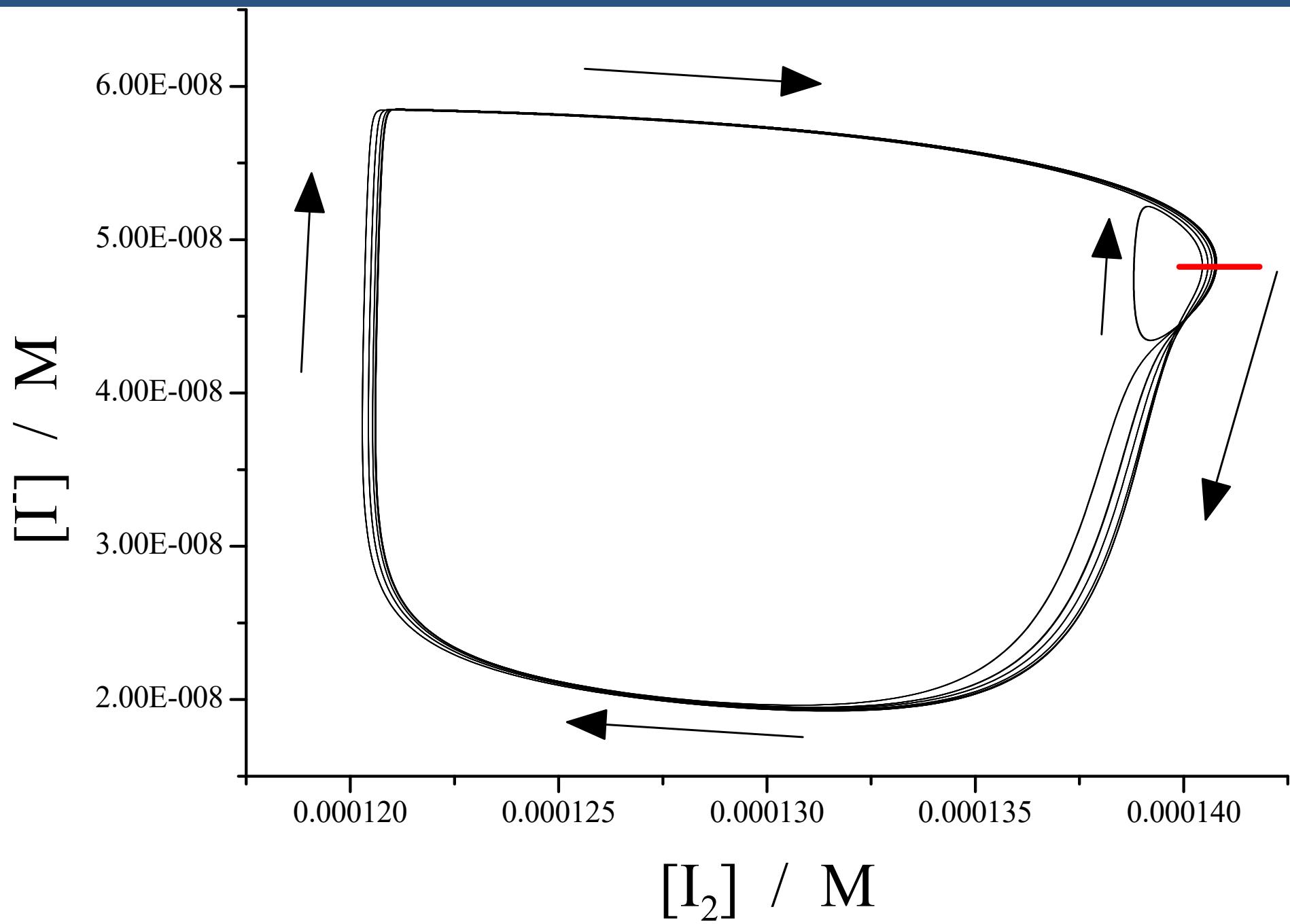
Periodični sistemi imaju diskretan mali broj tačaka u Poenkareovom preseku

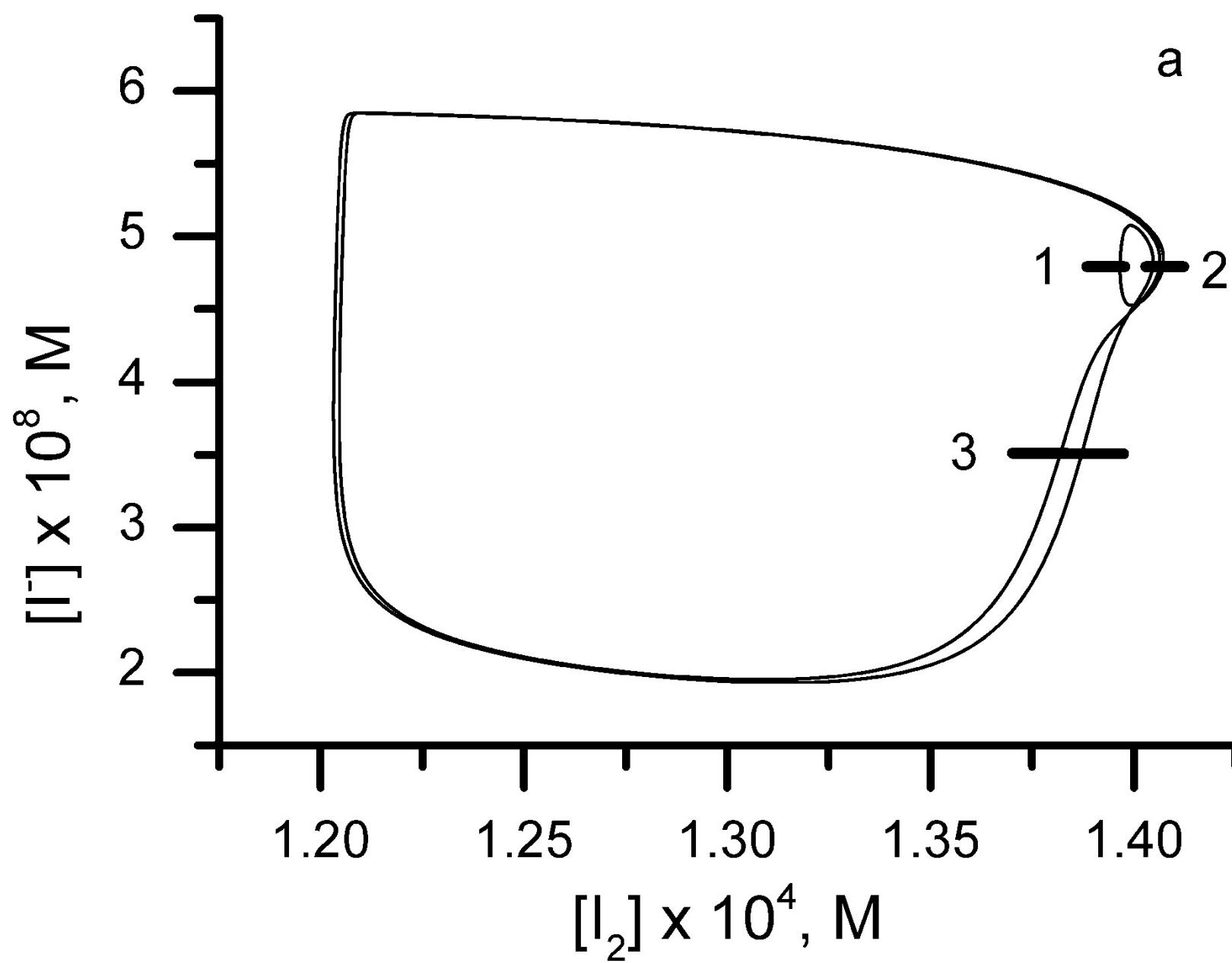
Haotični sistemi imaju “neograničen broj” tačaka u Poenkareovom preseku



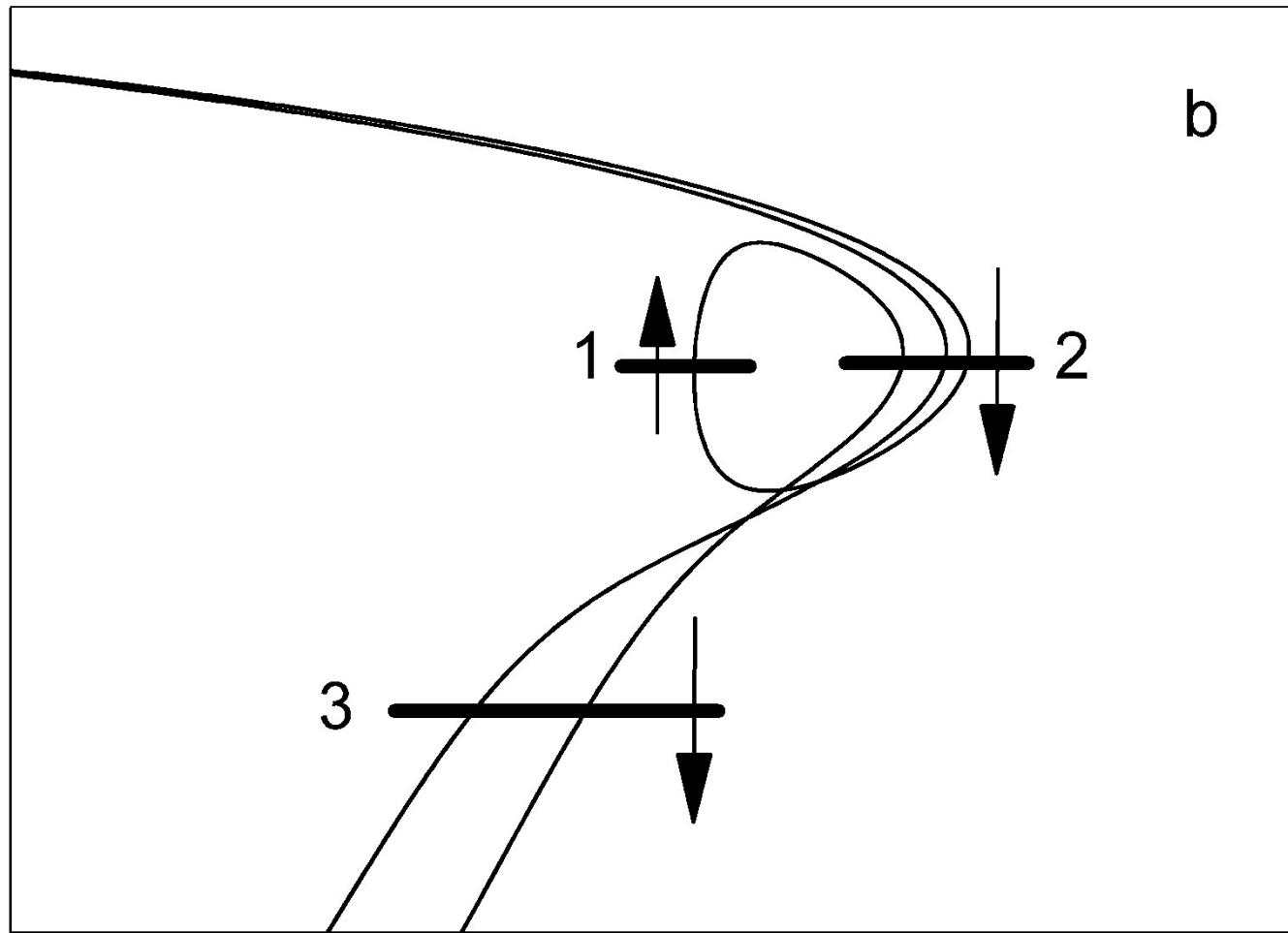
Izbor ravni preseka



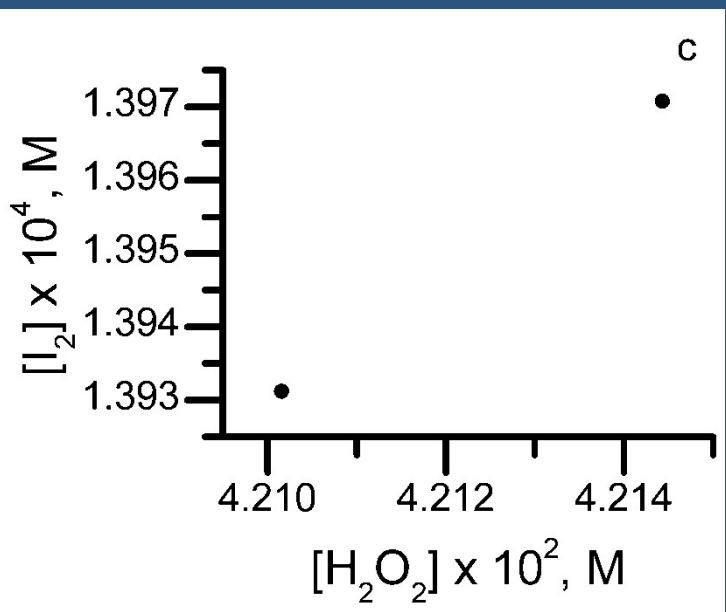




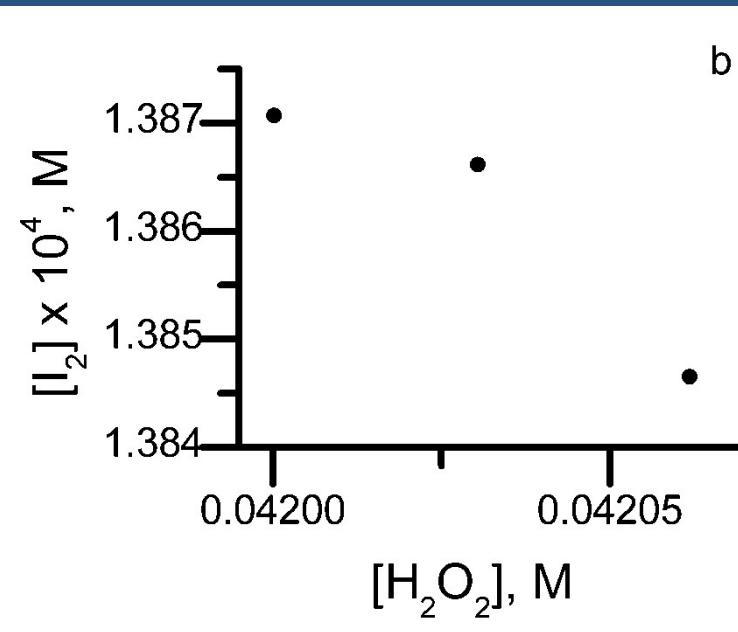
b



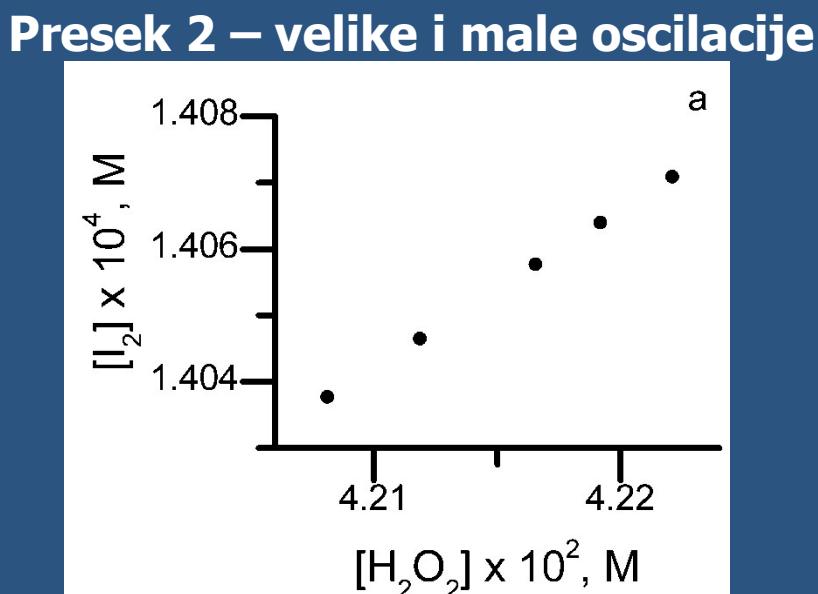
$$j_0 = 4.8550 \times 10^{-3} \text{ min}^{-1} \quad (2^{11})$$



Presek 1 – samo male oscilacije

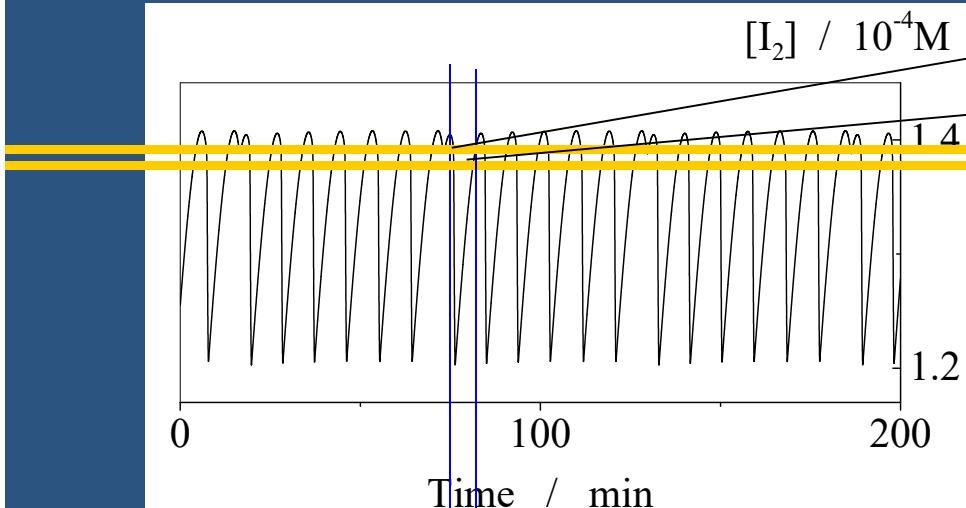


Presek 3 – samo velike oscilacije



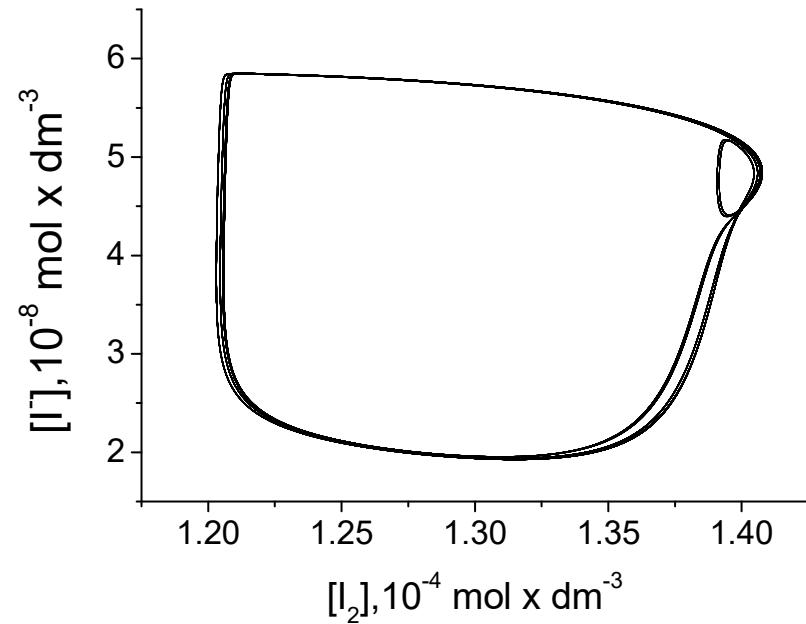
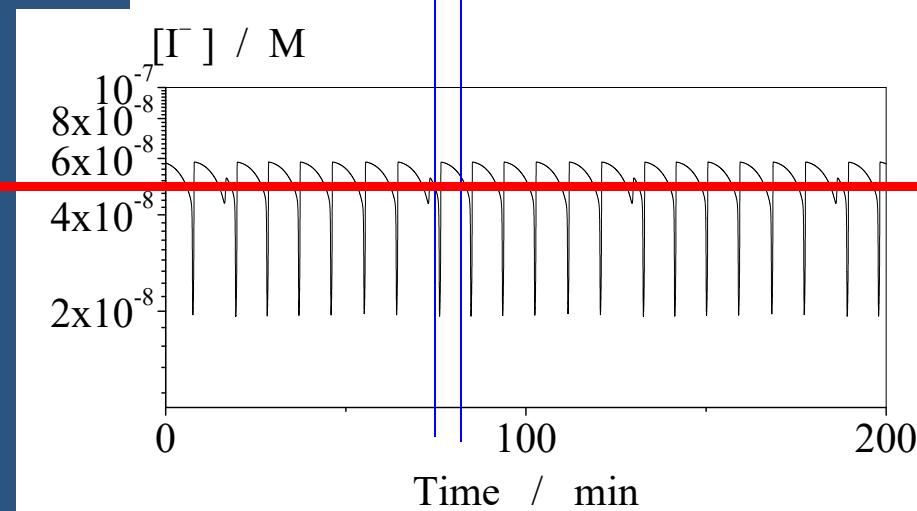
Presek 2 – velike i male oscilacije

Iteracione mape – povratne mape



$$[I_2]_n$$

$$[I_2]_{n+1}$$

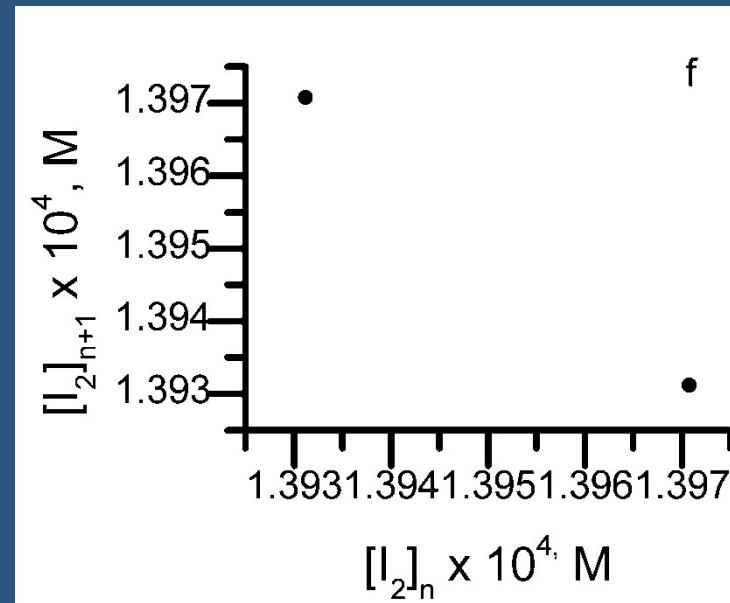
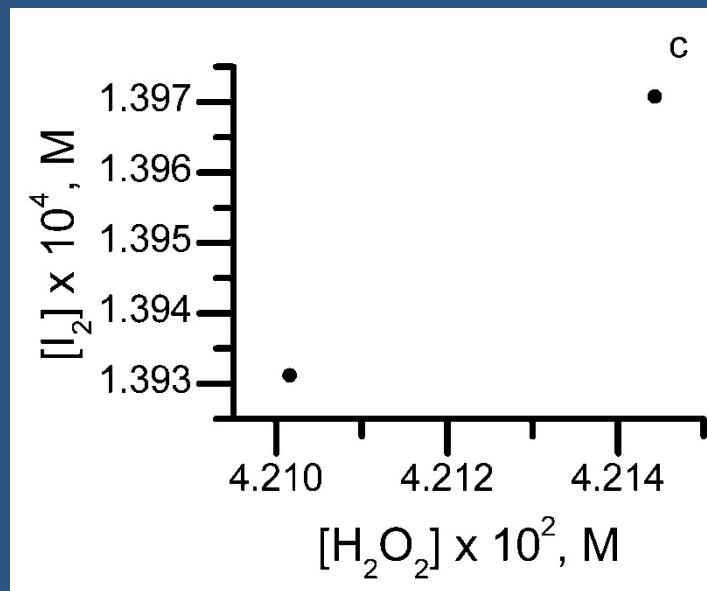


Iteracione mape – povratne mape

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



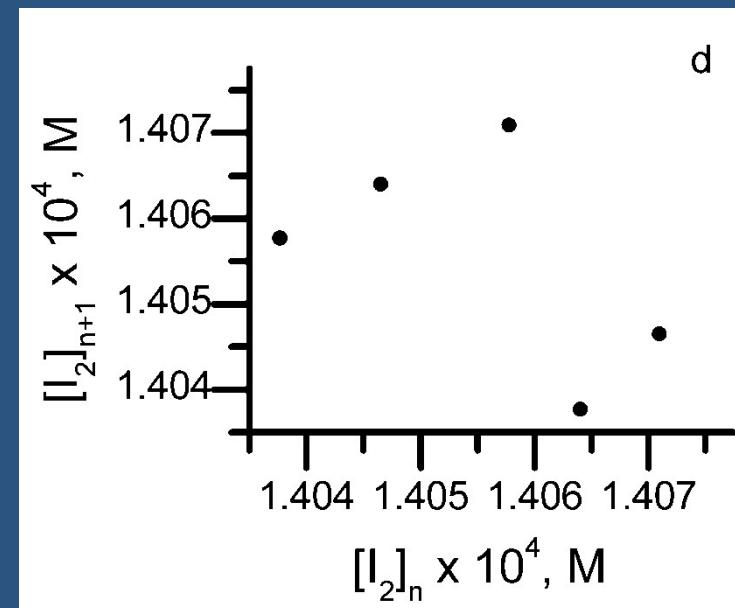
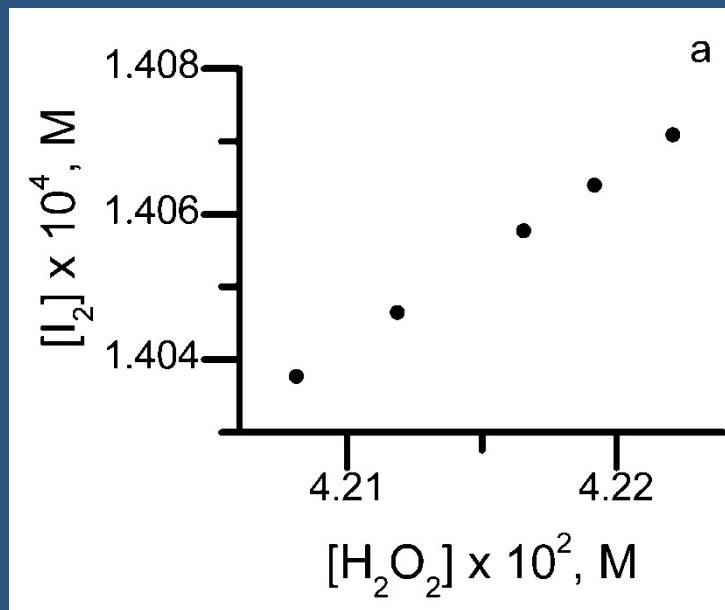
Poenkareova iteraciona mapa

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 2 – male i velike oscilacije



Poenkareov presek



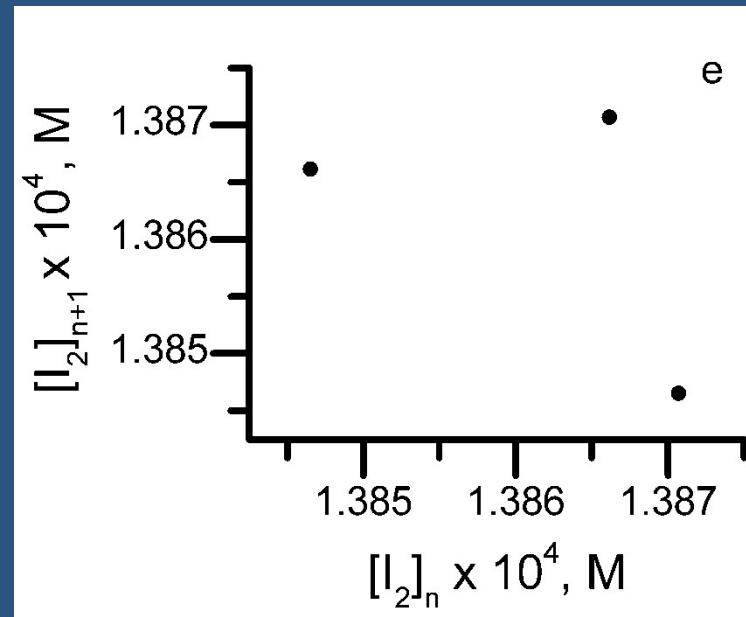
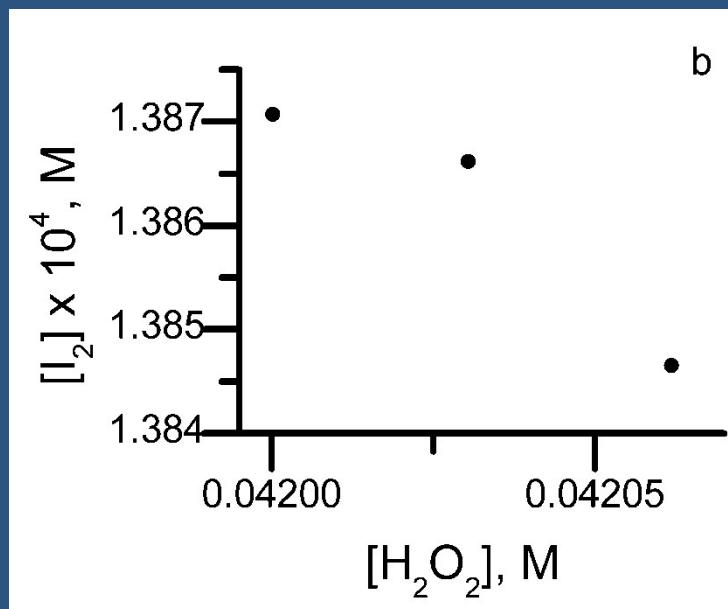
Poenkareova iteraciona mapa

Iteracione mape – povratne mape

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

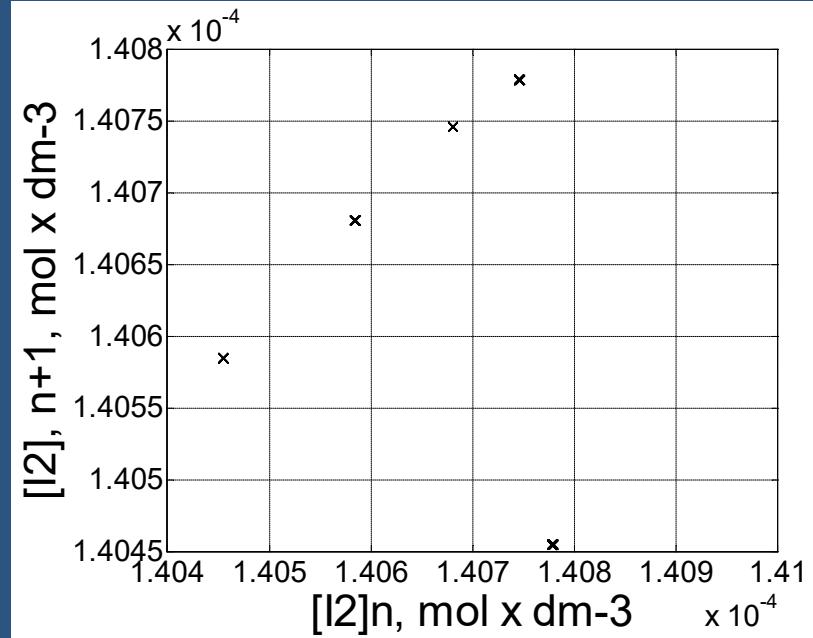
$$j_0 = 4.8550 \times 10^{-3} \text{ min}^{-1} \quad (2^1 1^1)$$

Presek 3 – samo velike oscilacije

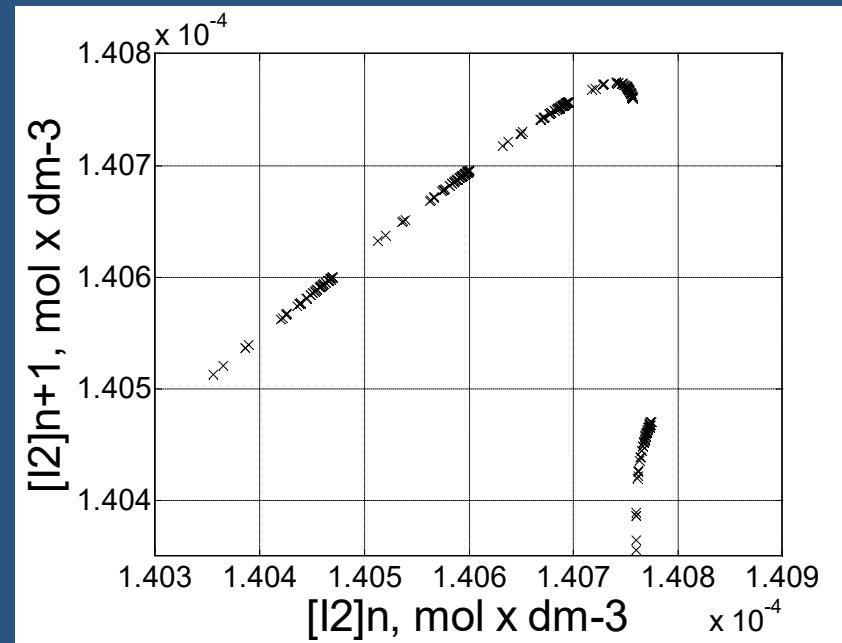


Poenkareov presek

Poenkareova iteraciona mapa

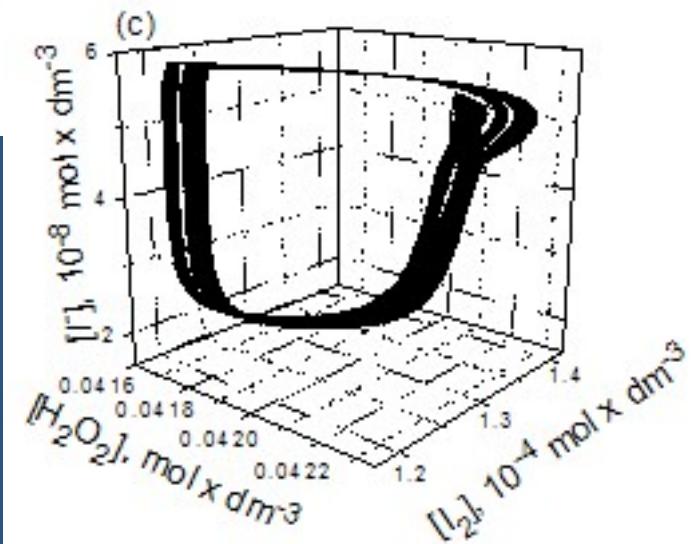
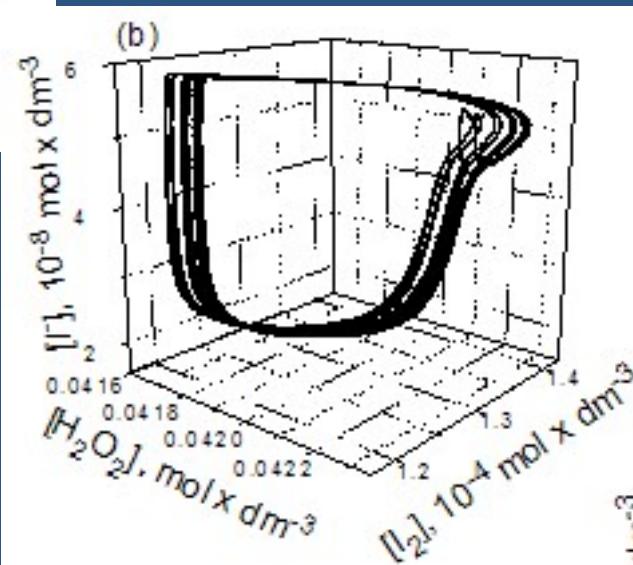
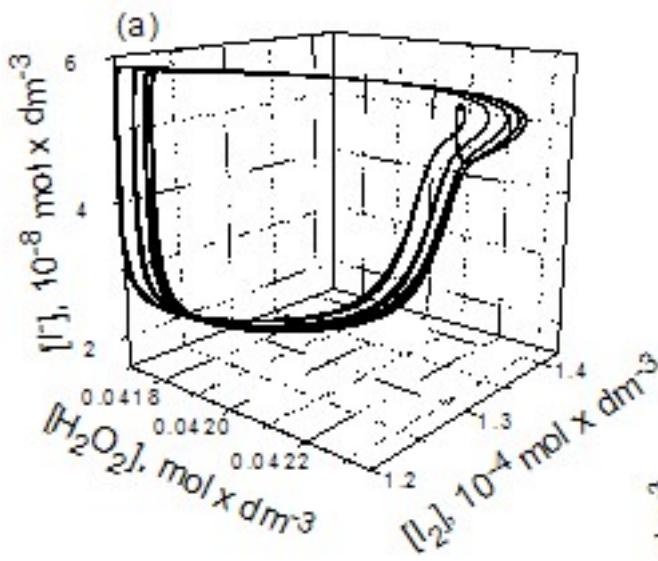


Periodika



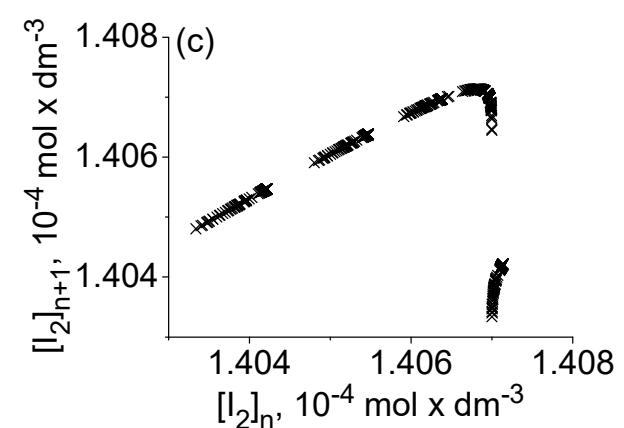
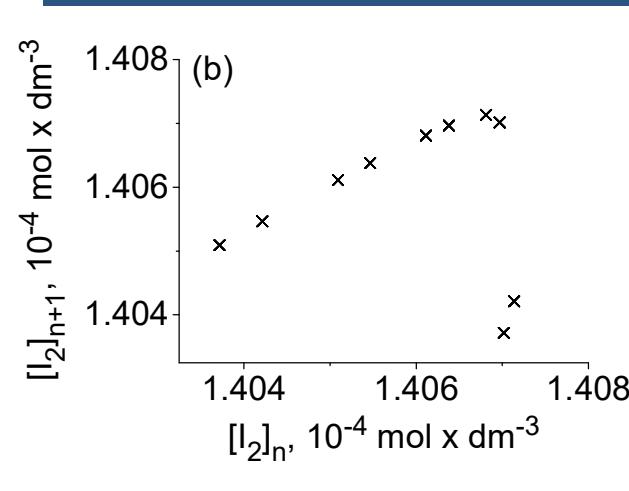
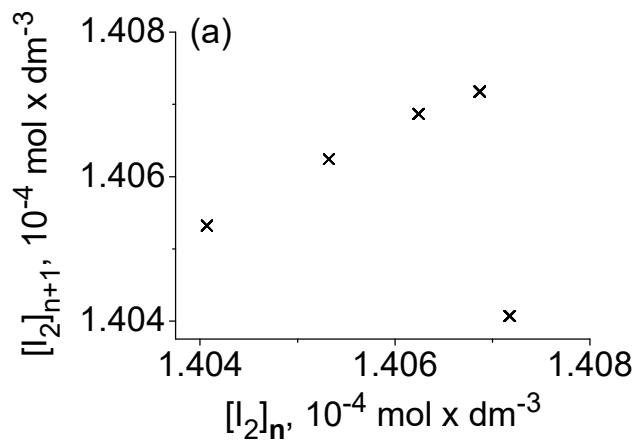
Haos

Udvajanje perioda – scenario nastanka haosa

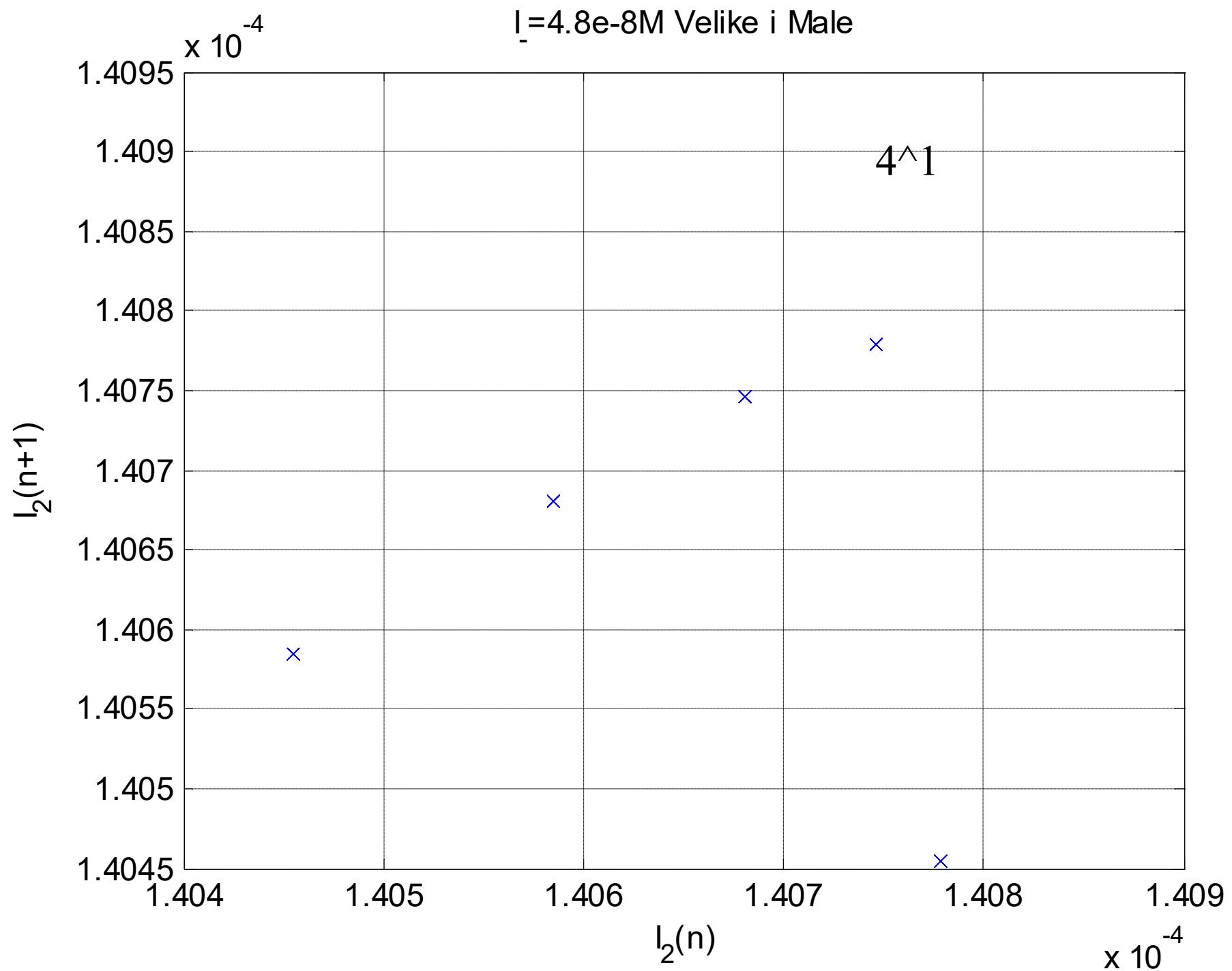


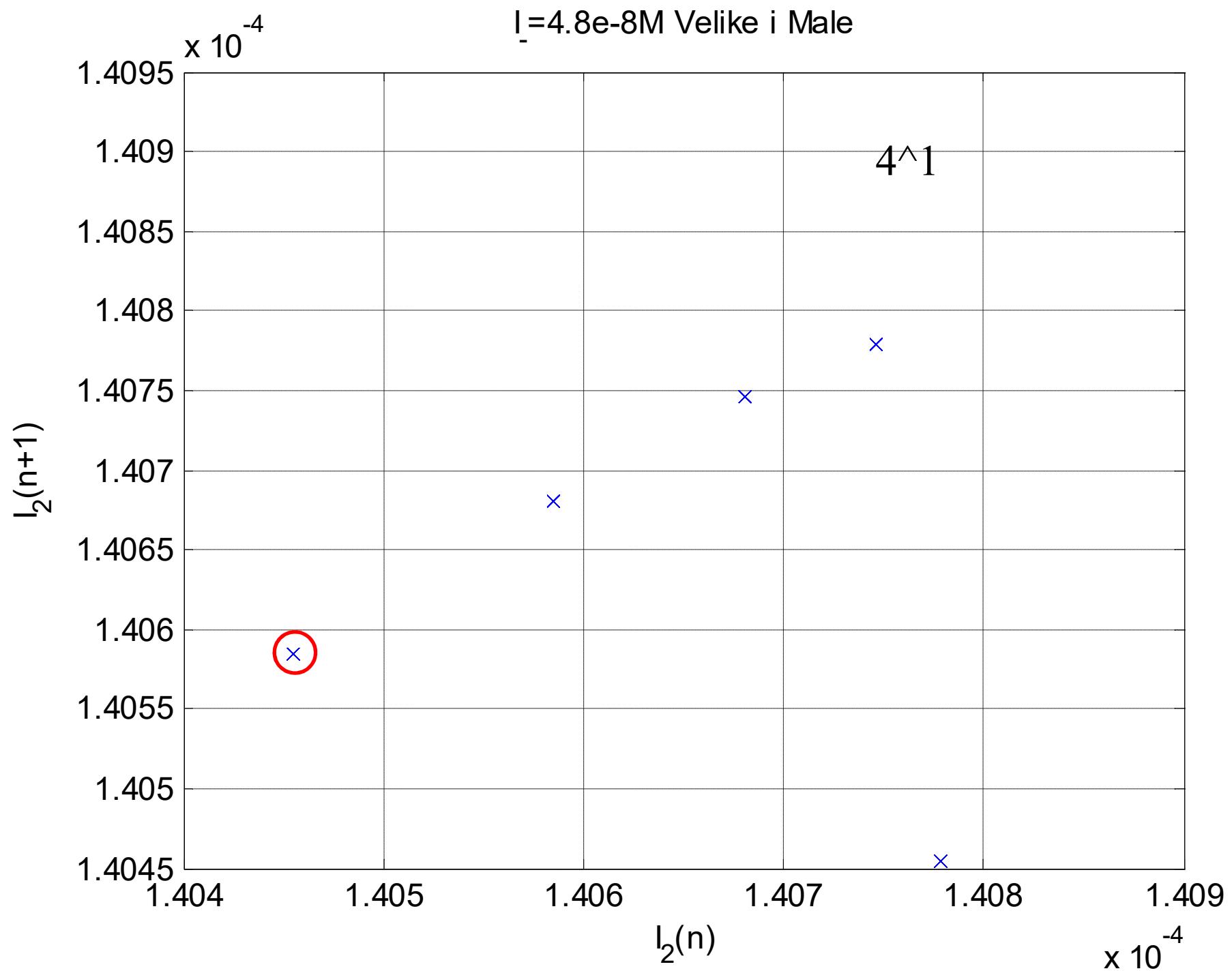
Prikaz atraktora
u faznom prostoru

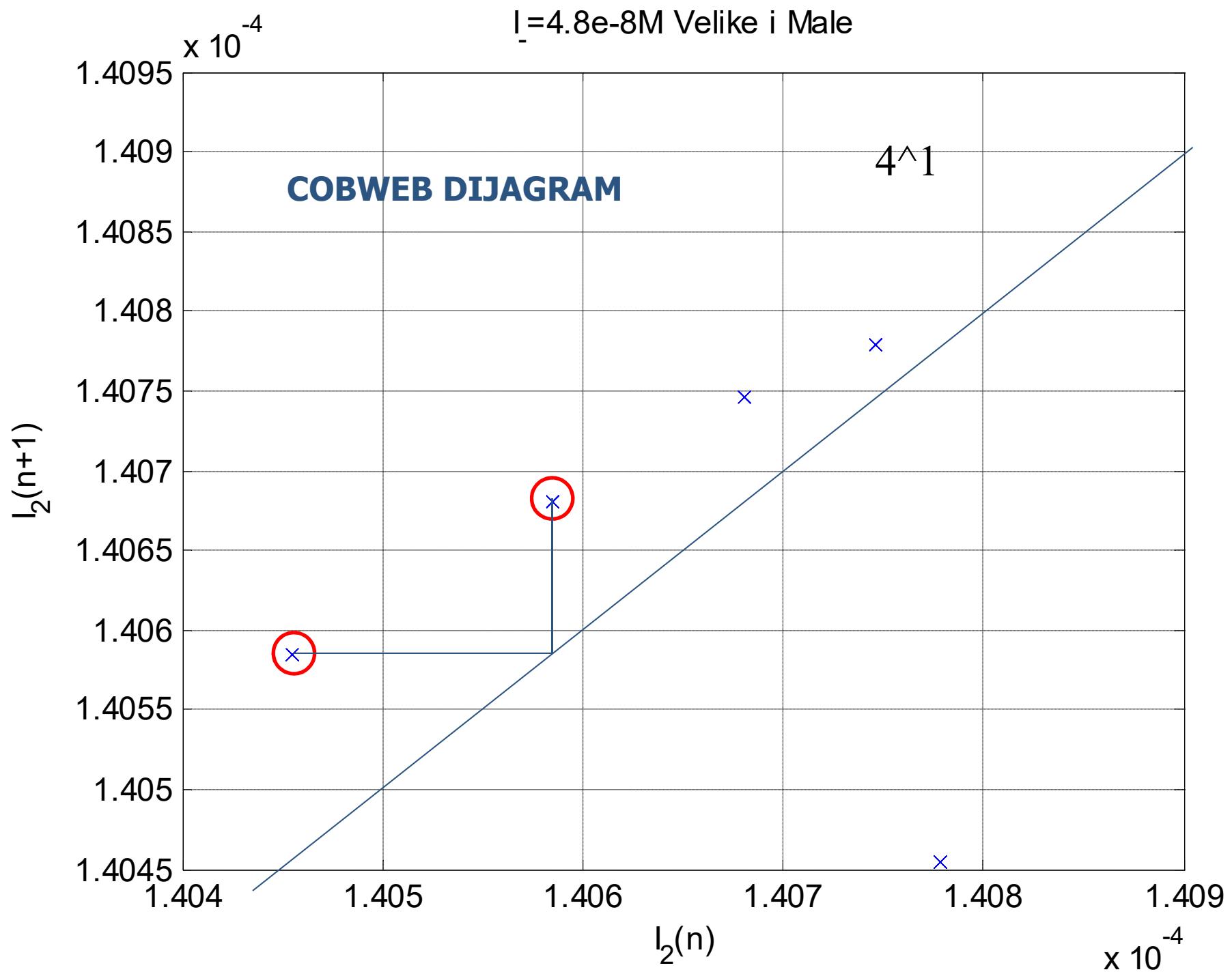
Udvajanje perioda – scenario nastanka haosa

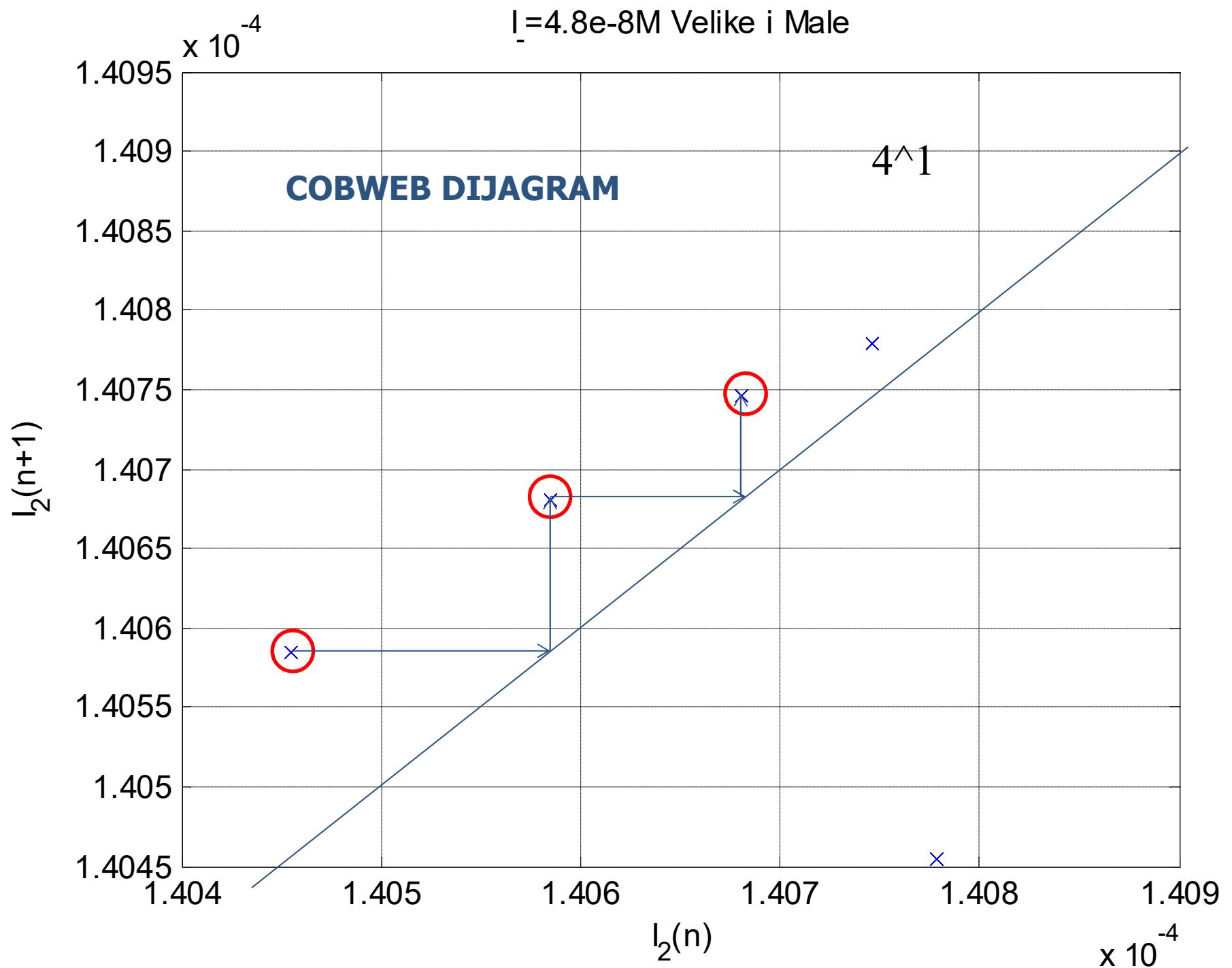


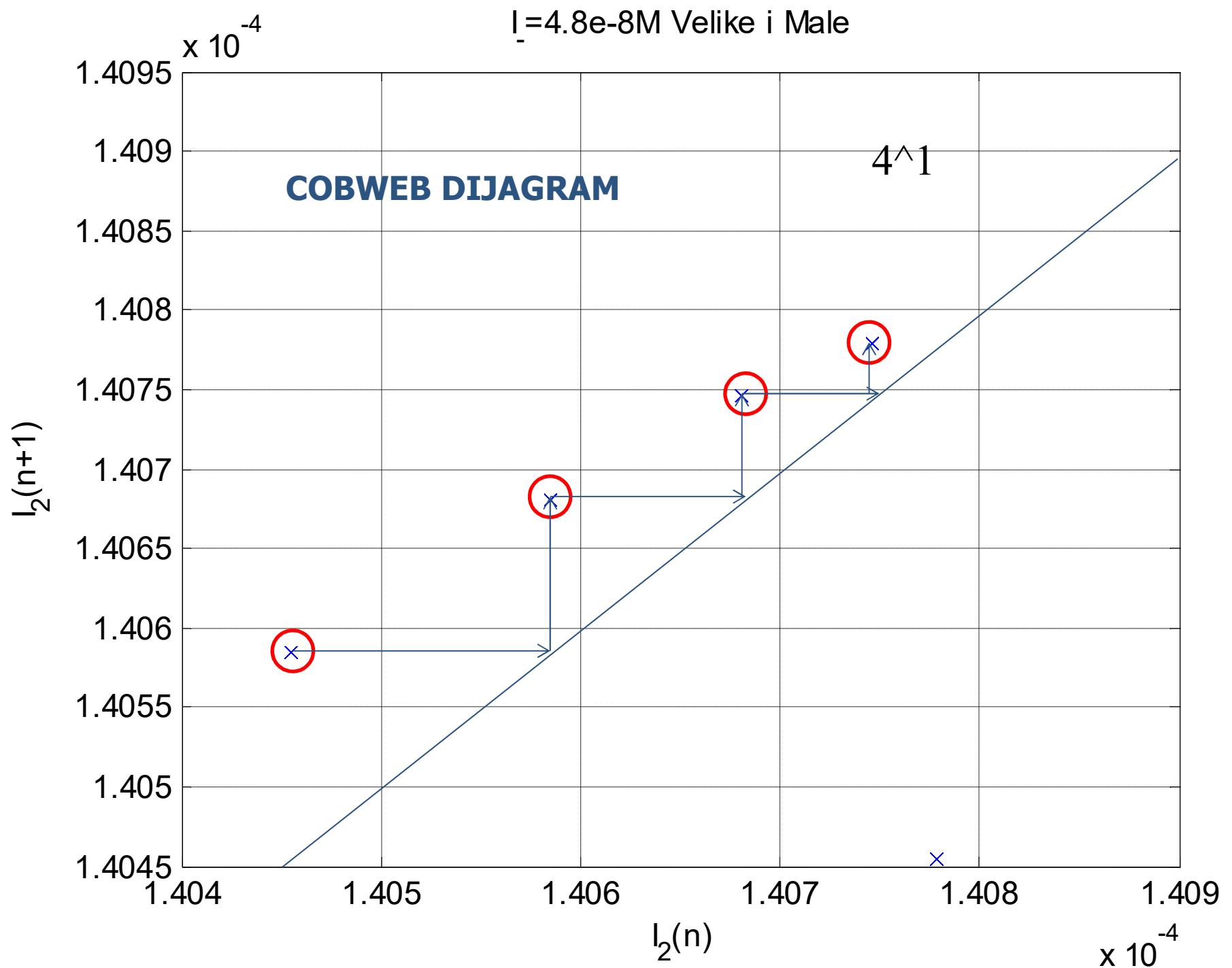
Prikaz Jednodimenzionih
Mapa Poenkareovog preseka
atraktora

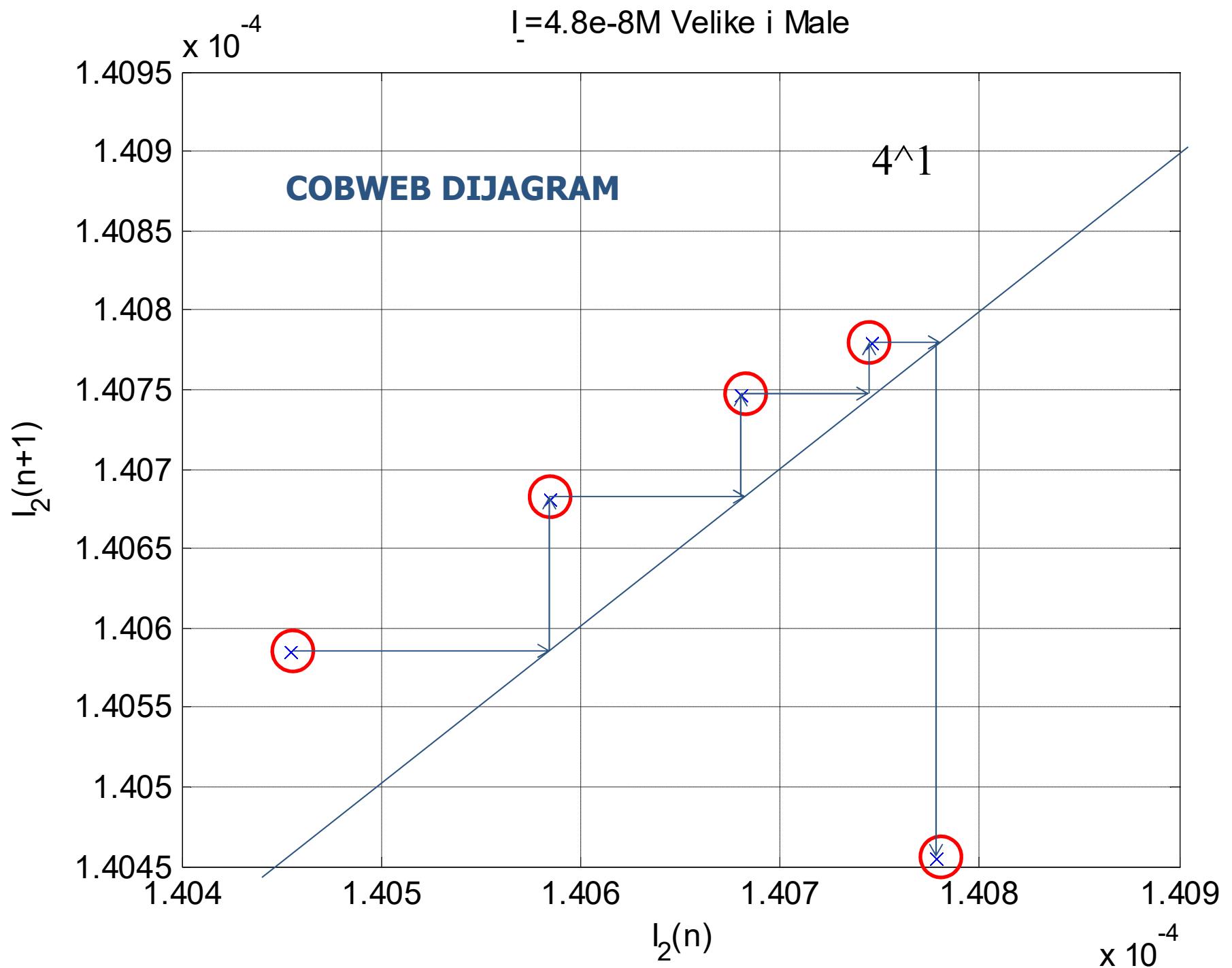


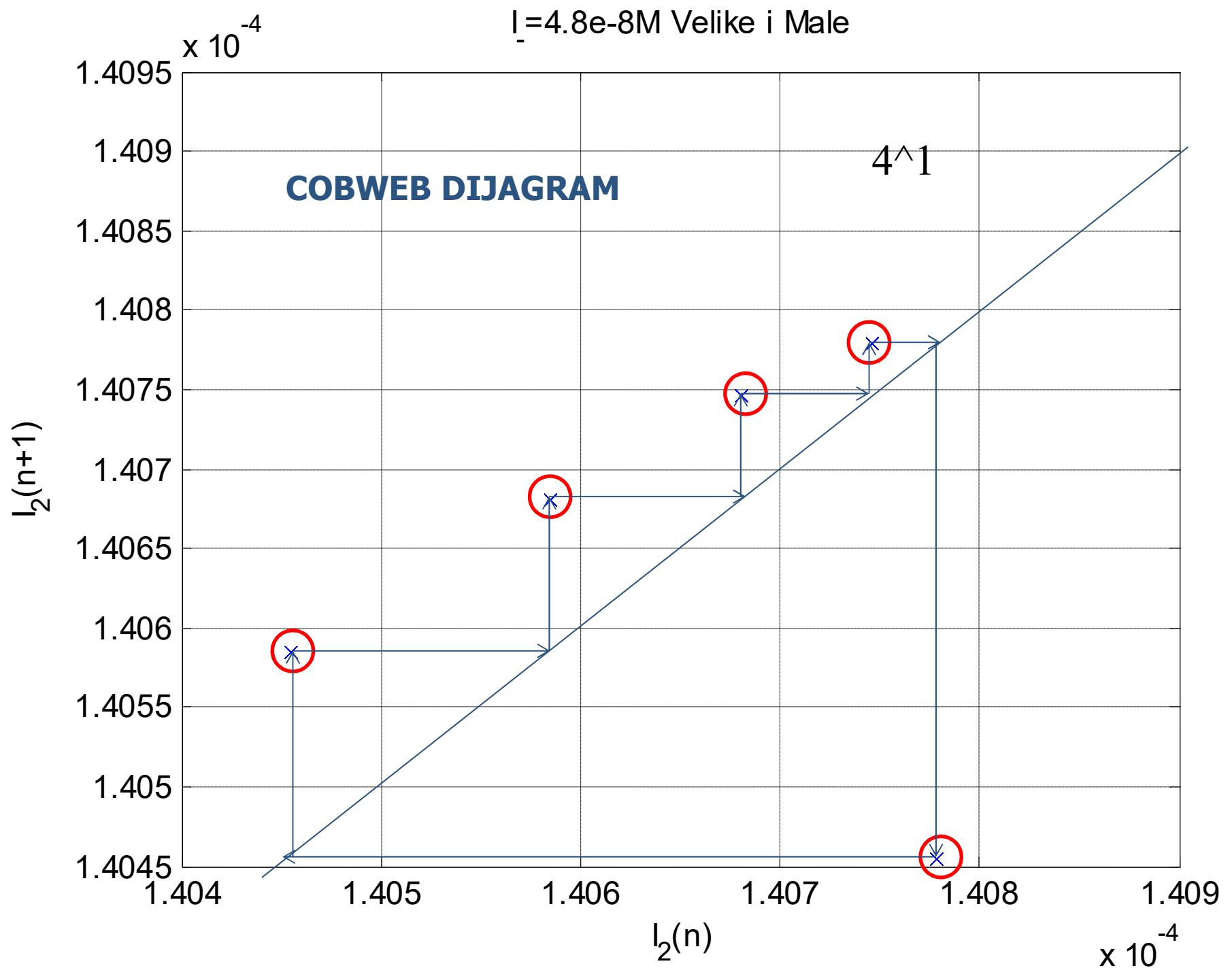


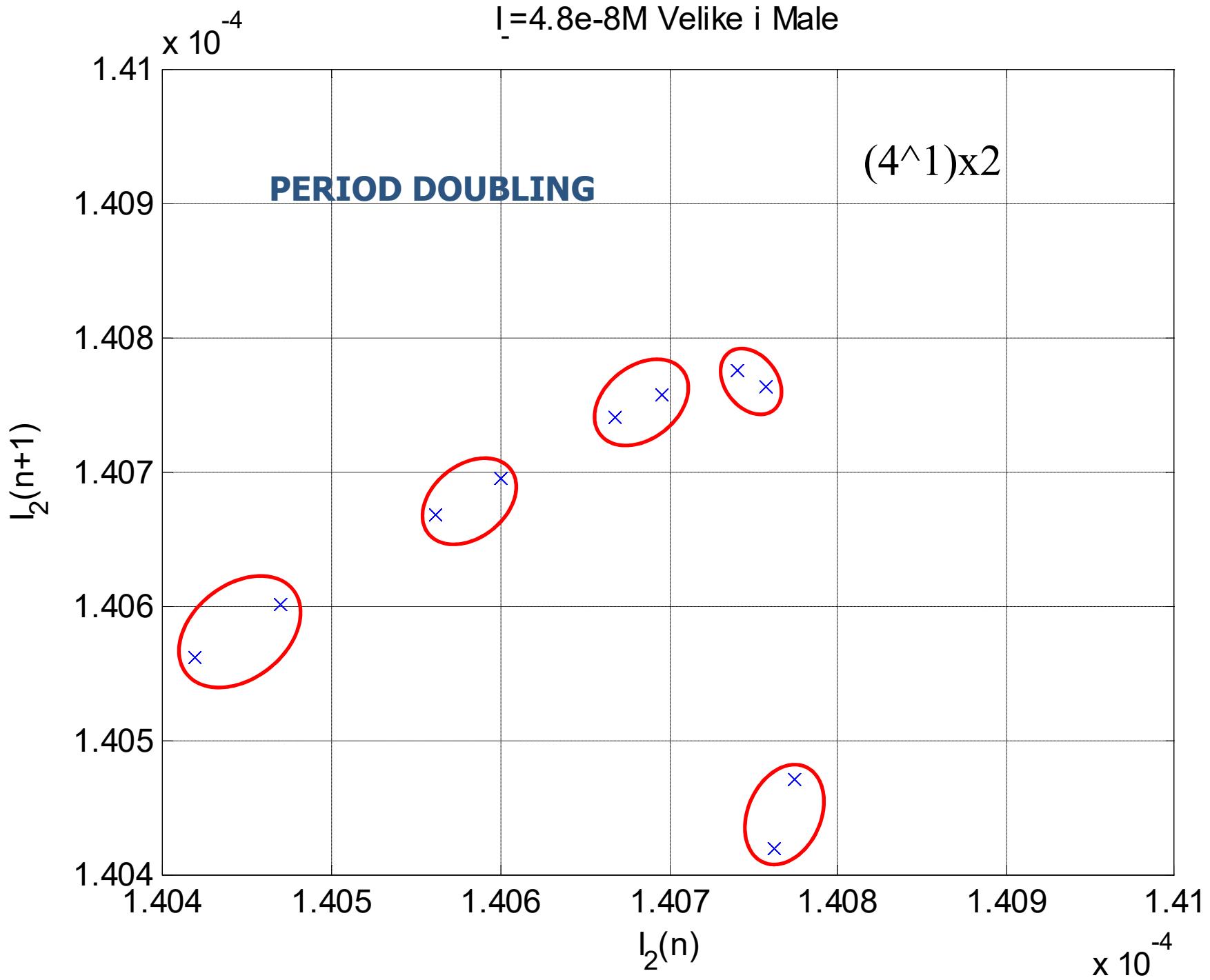


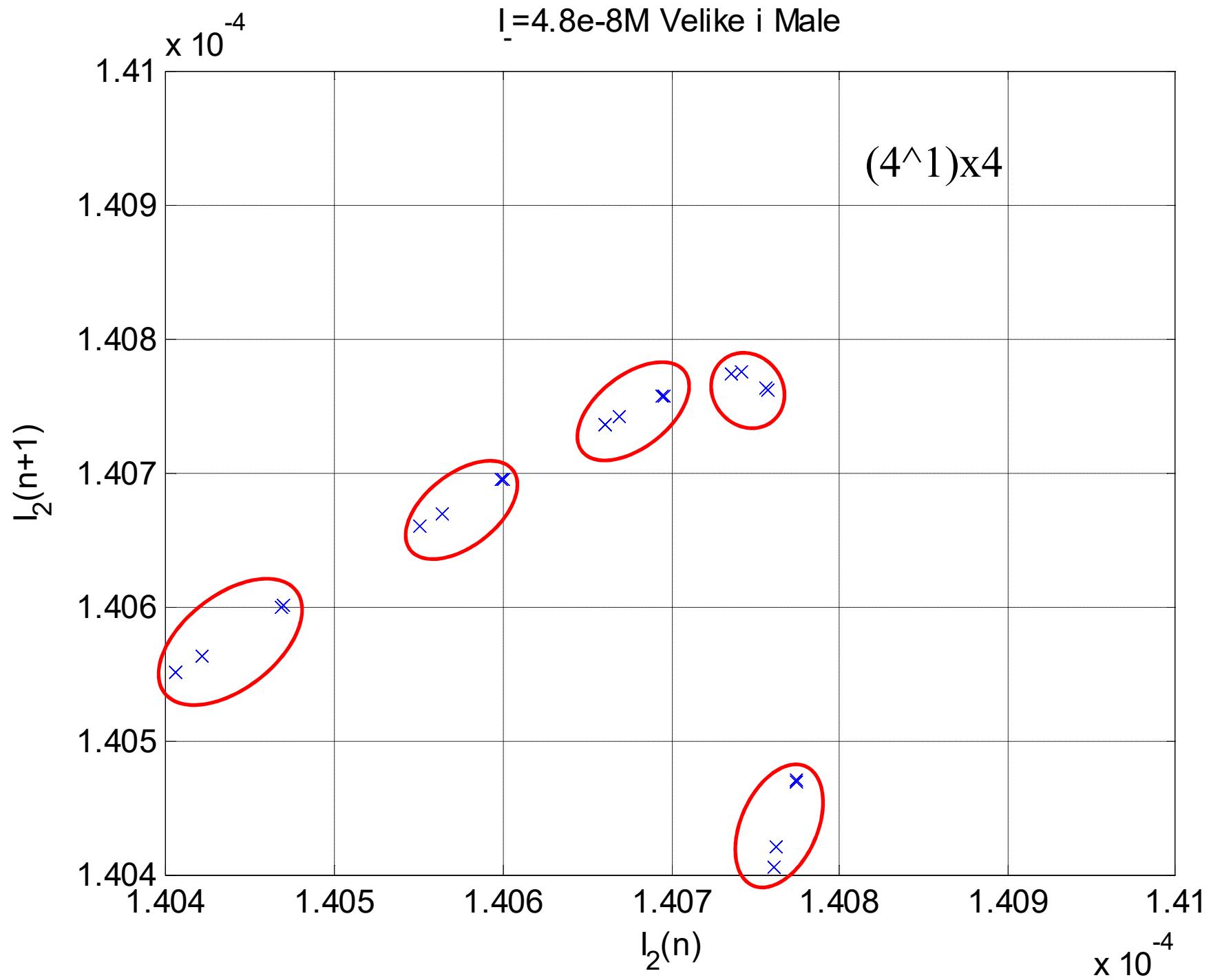


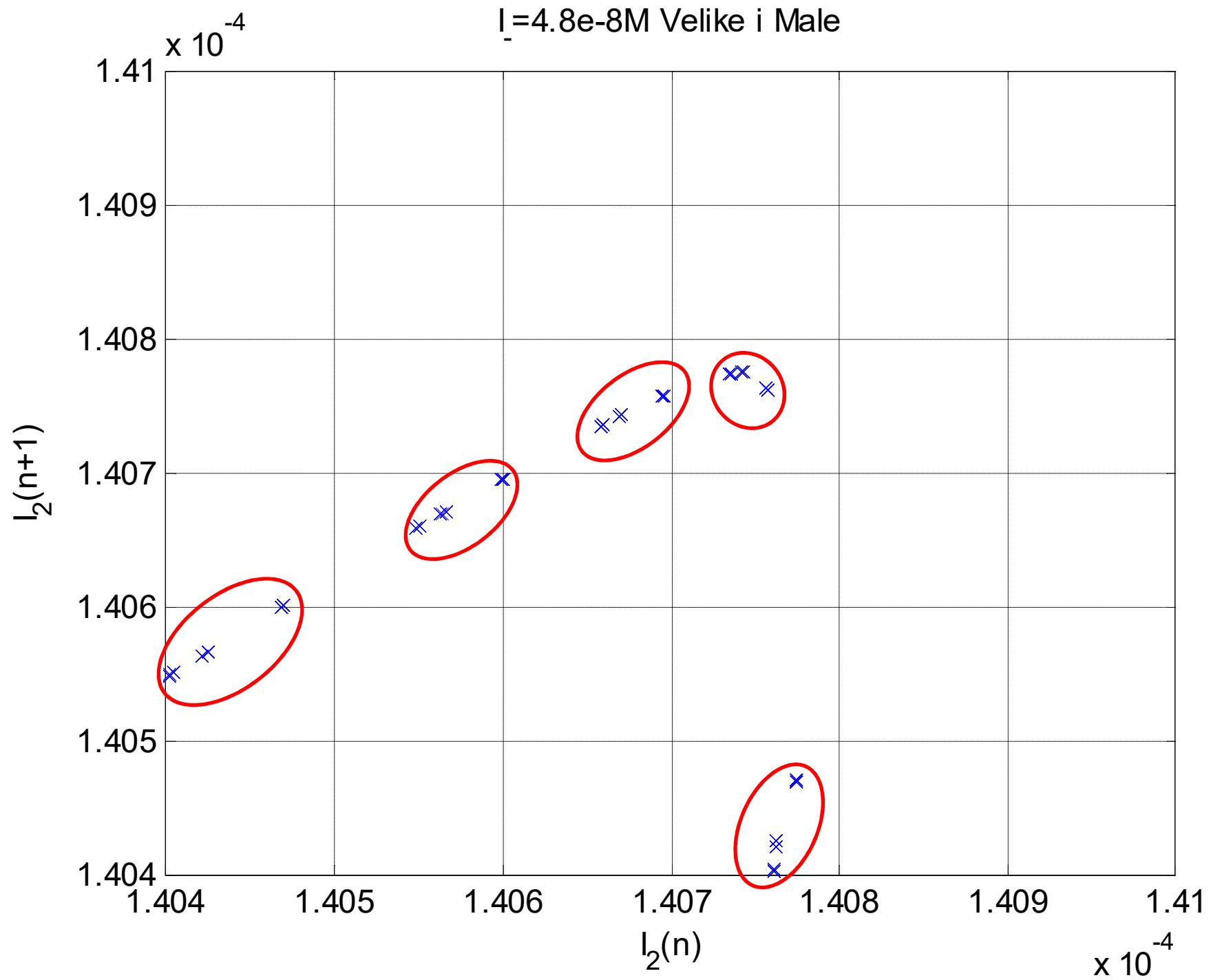


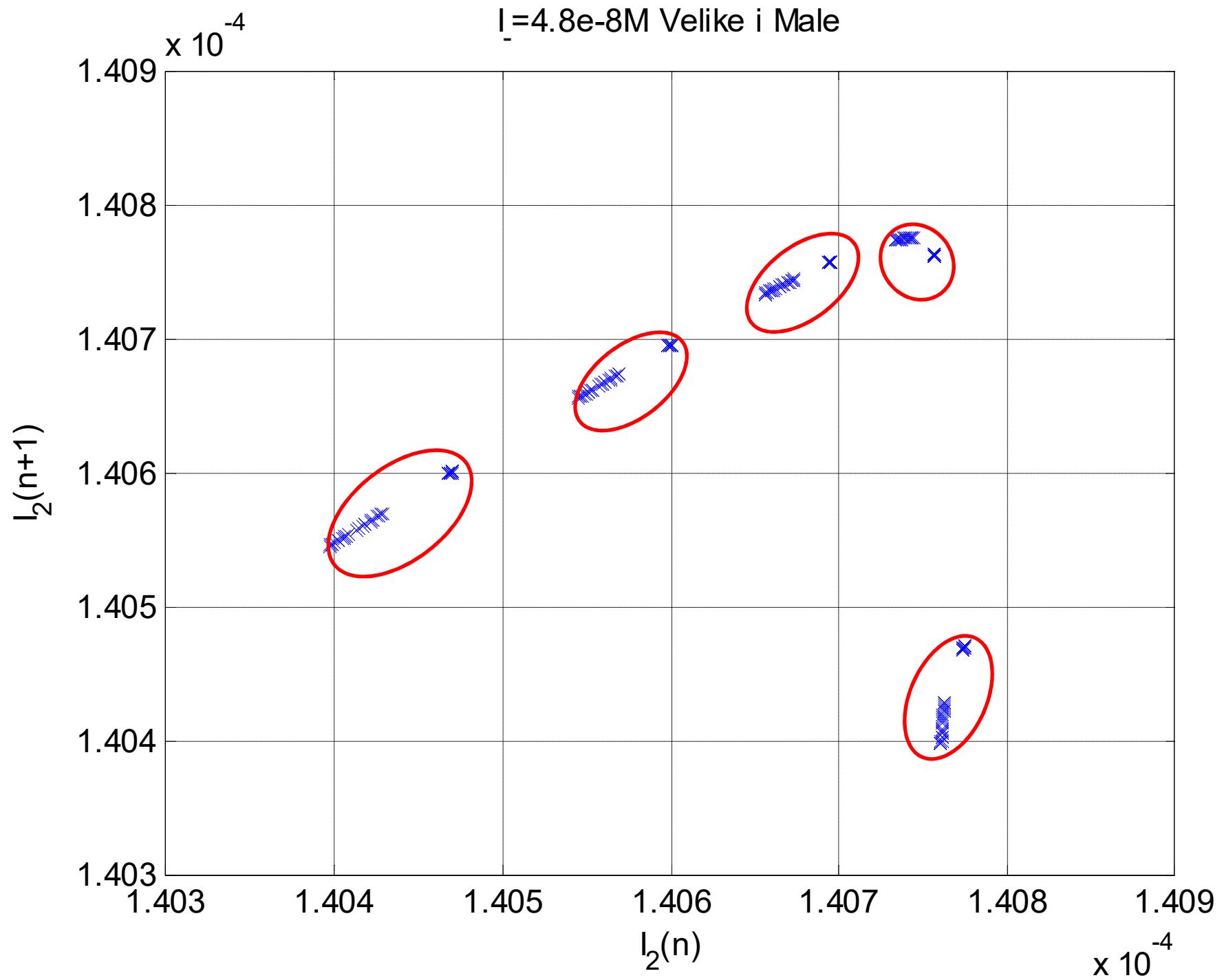


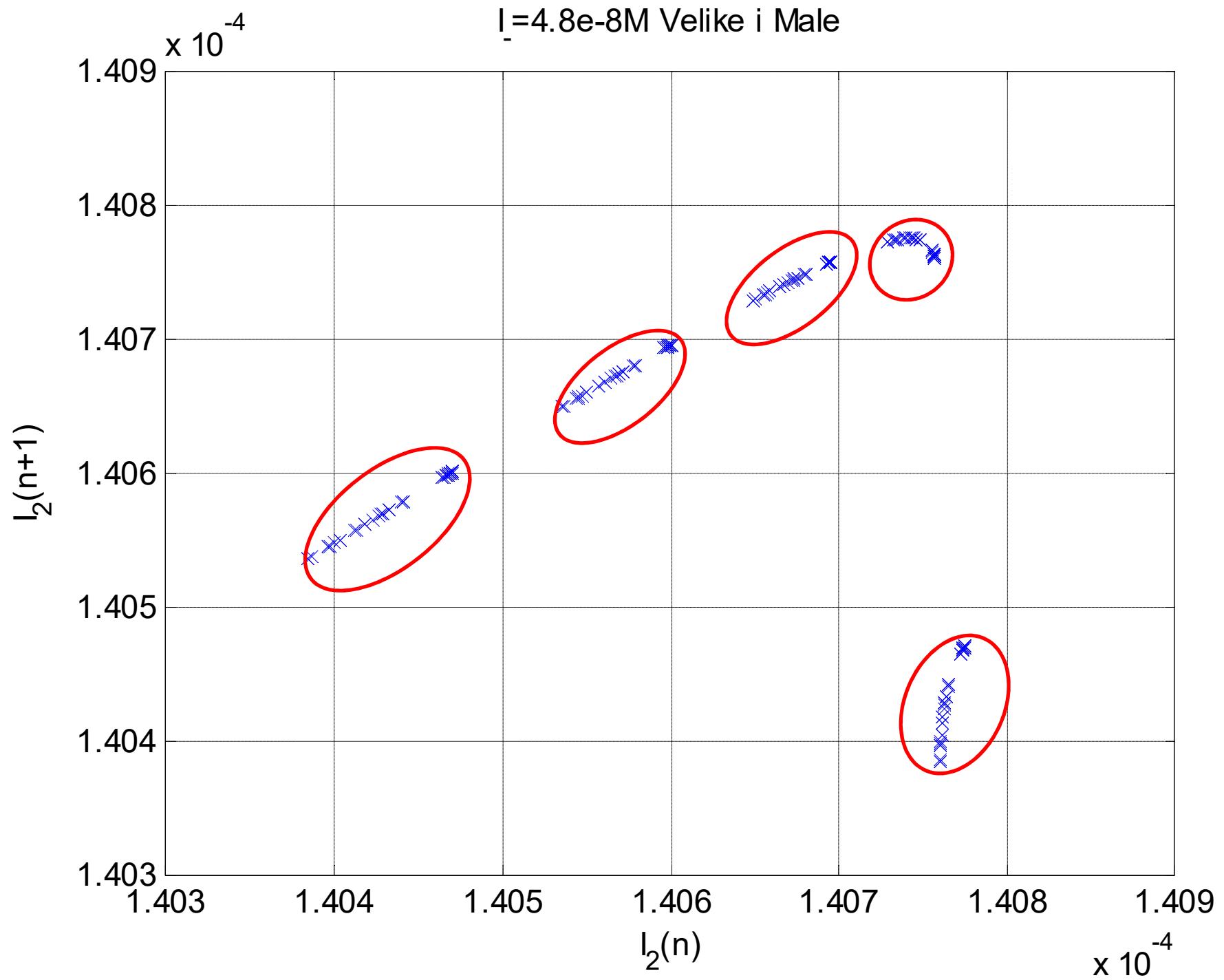


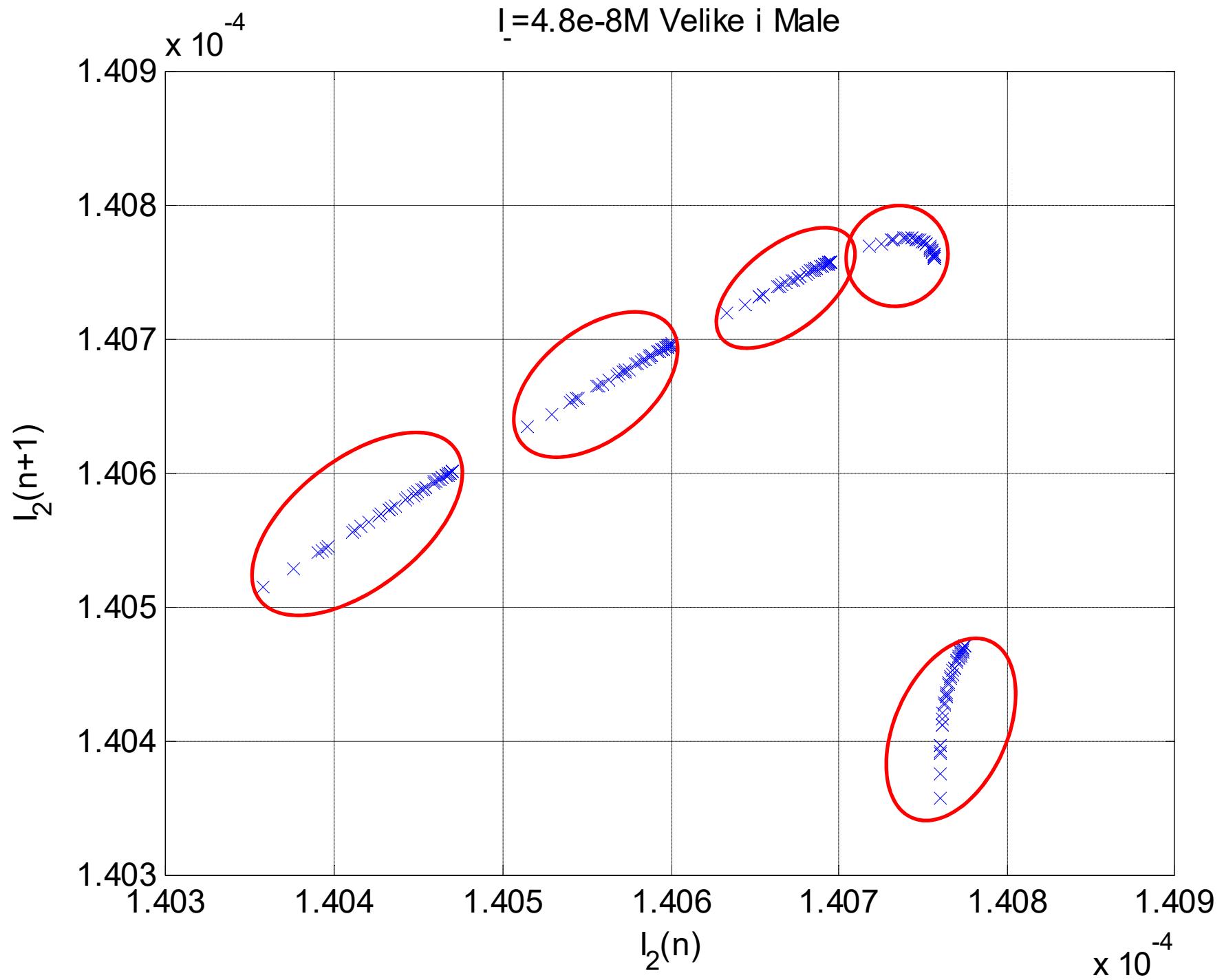


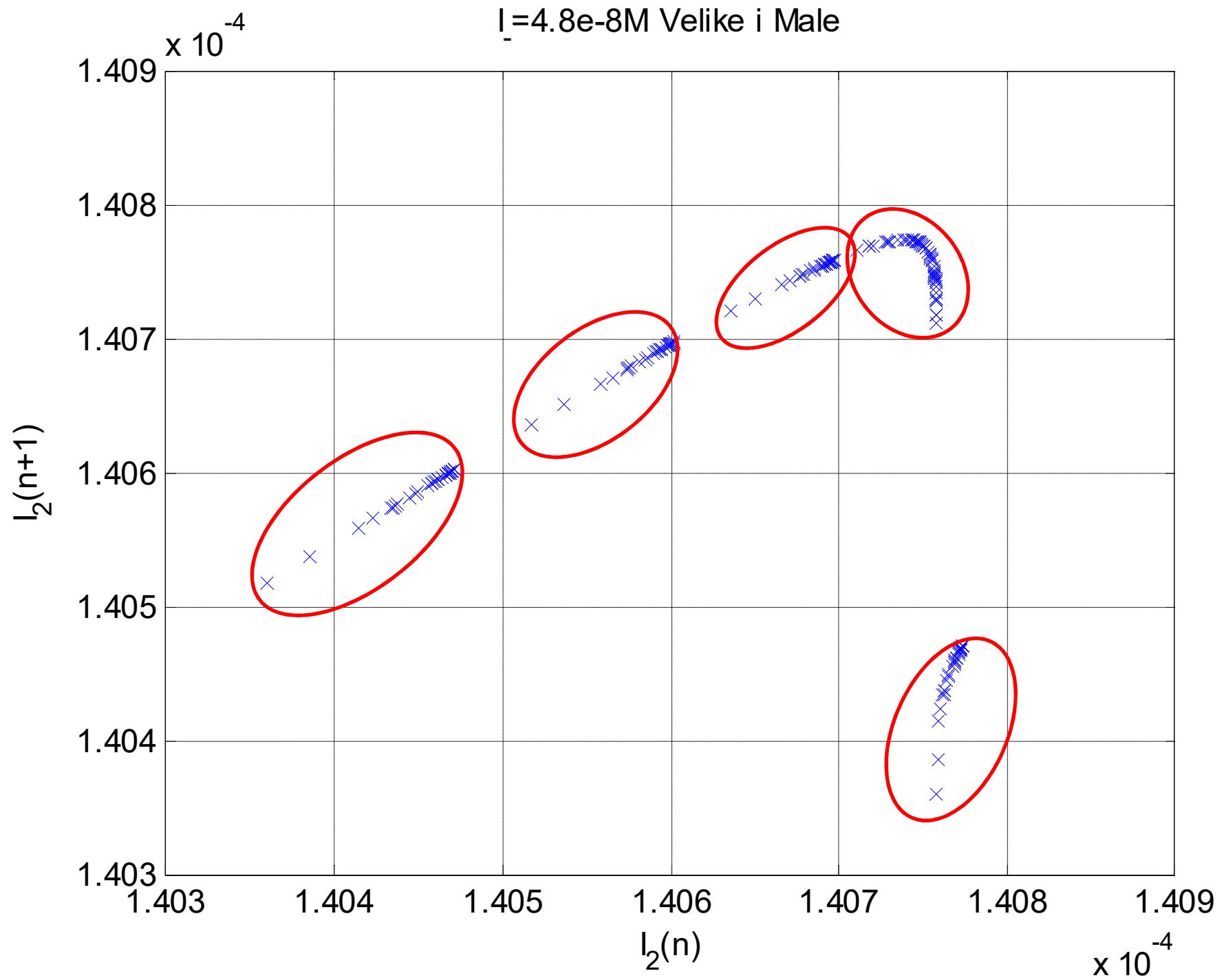


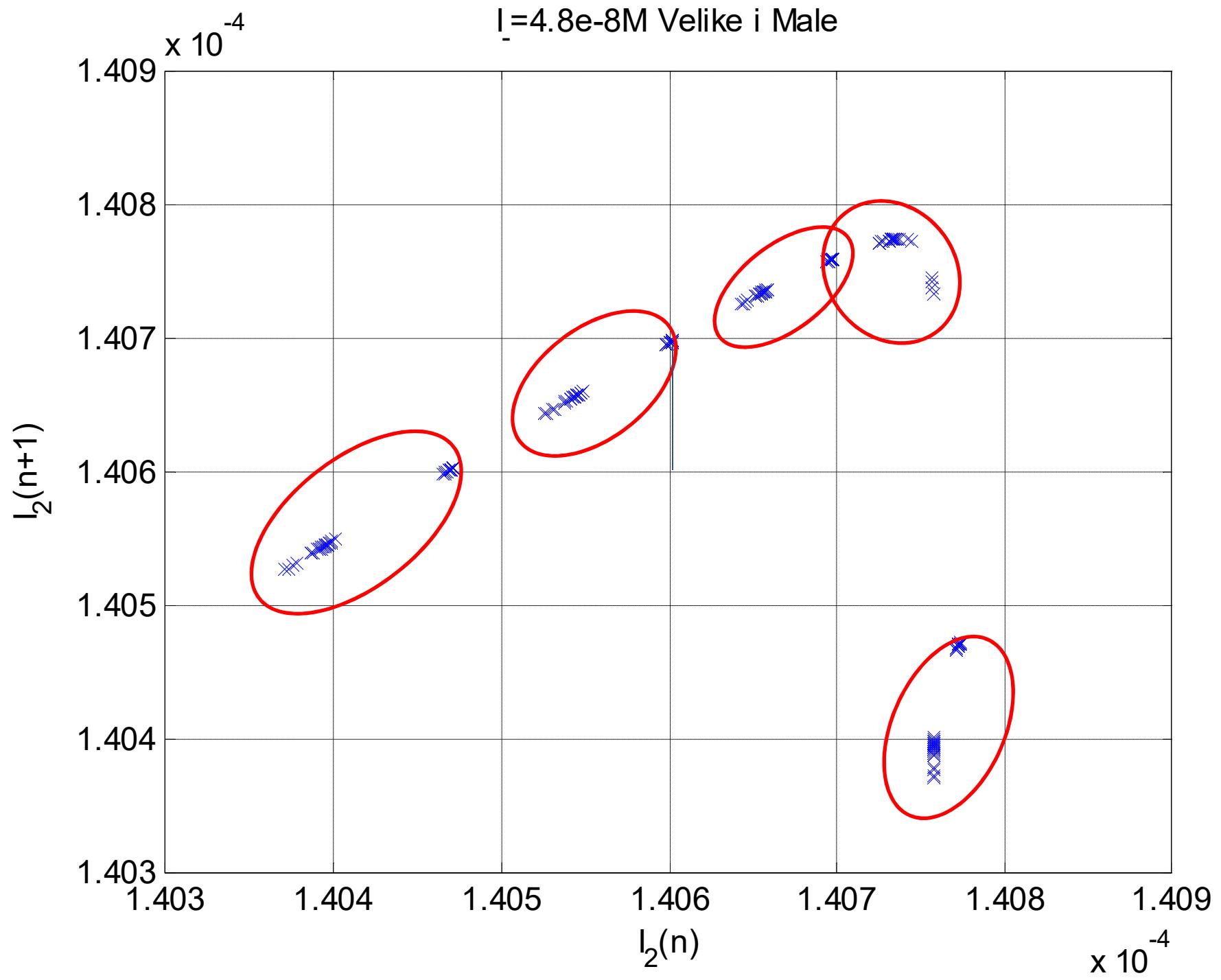


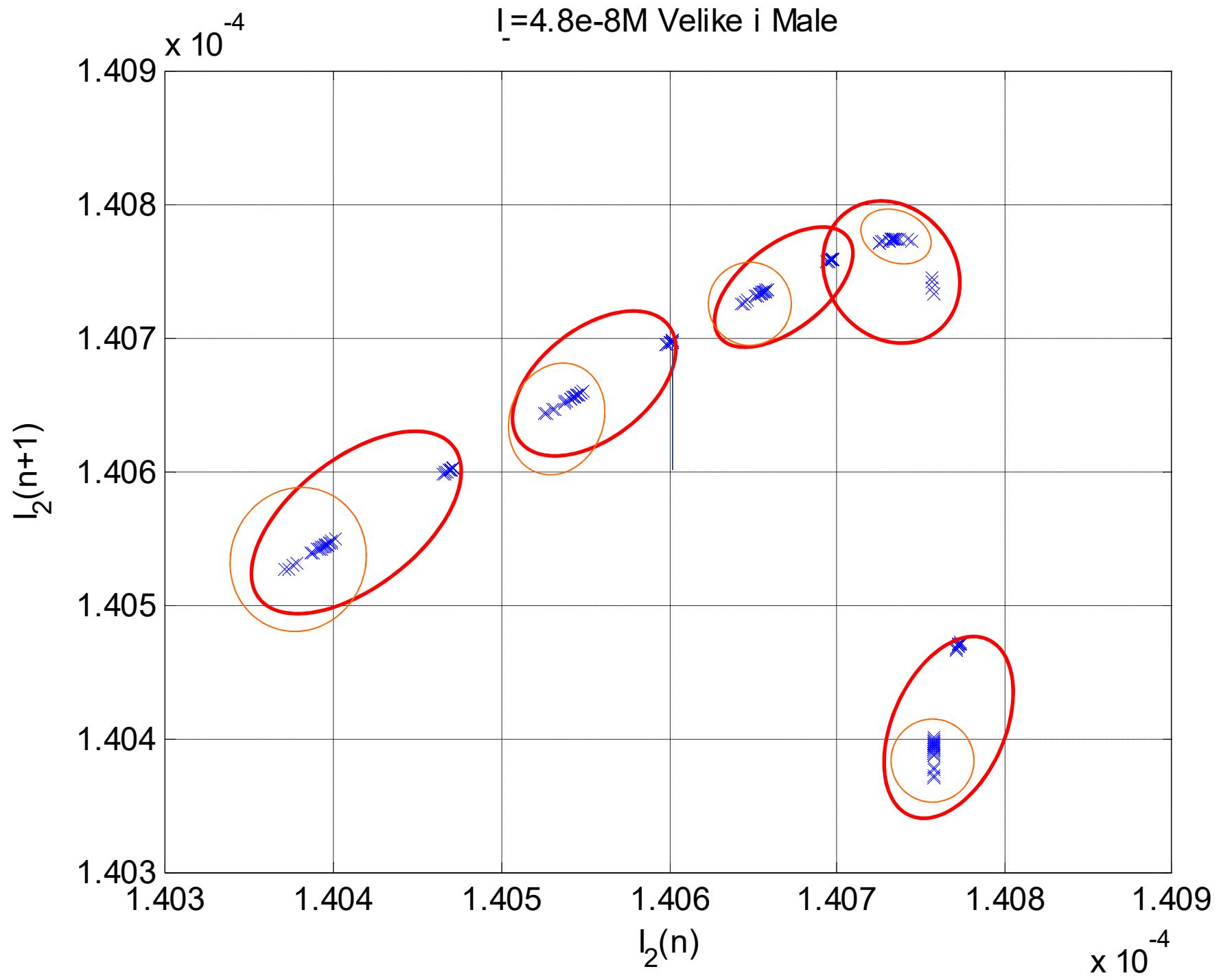


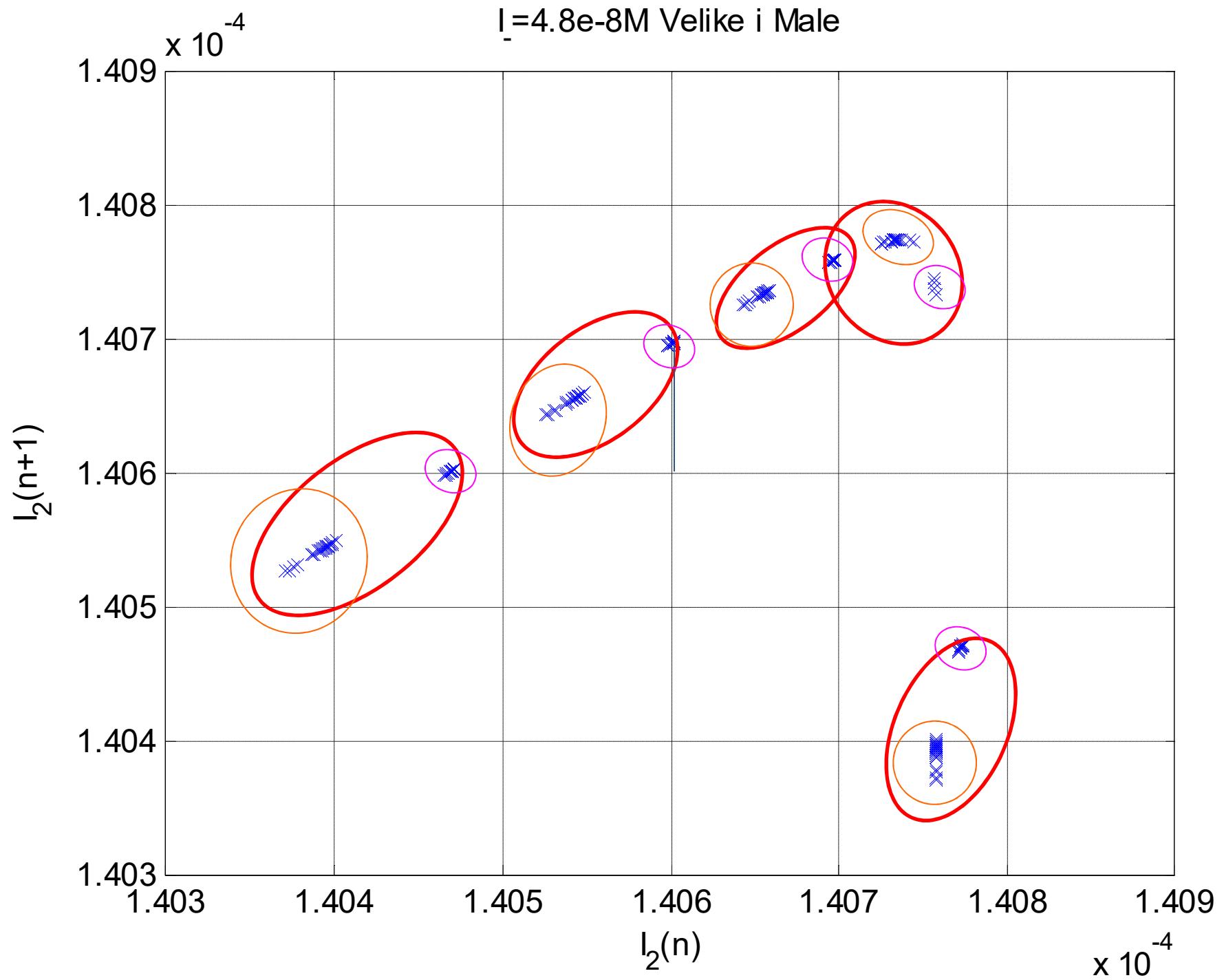


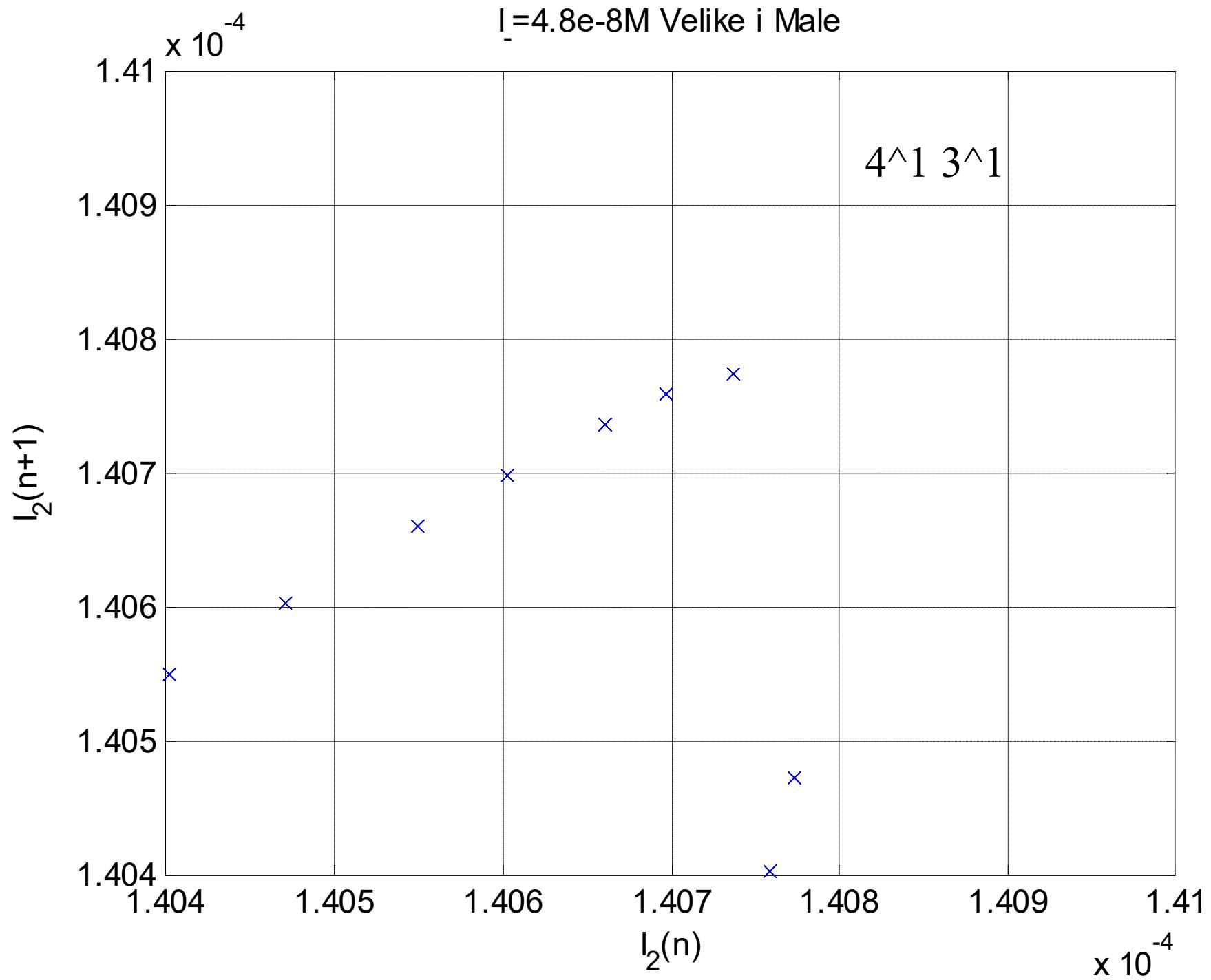


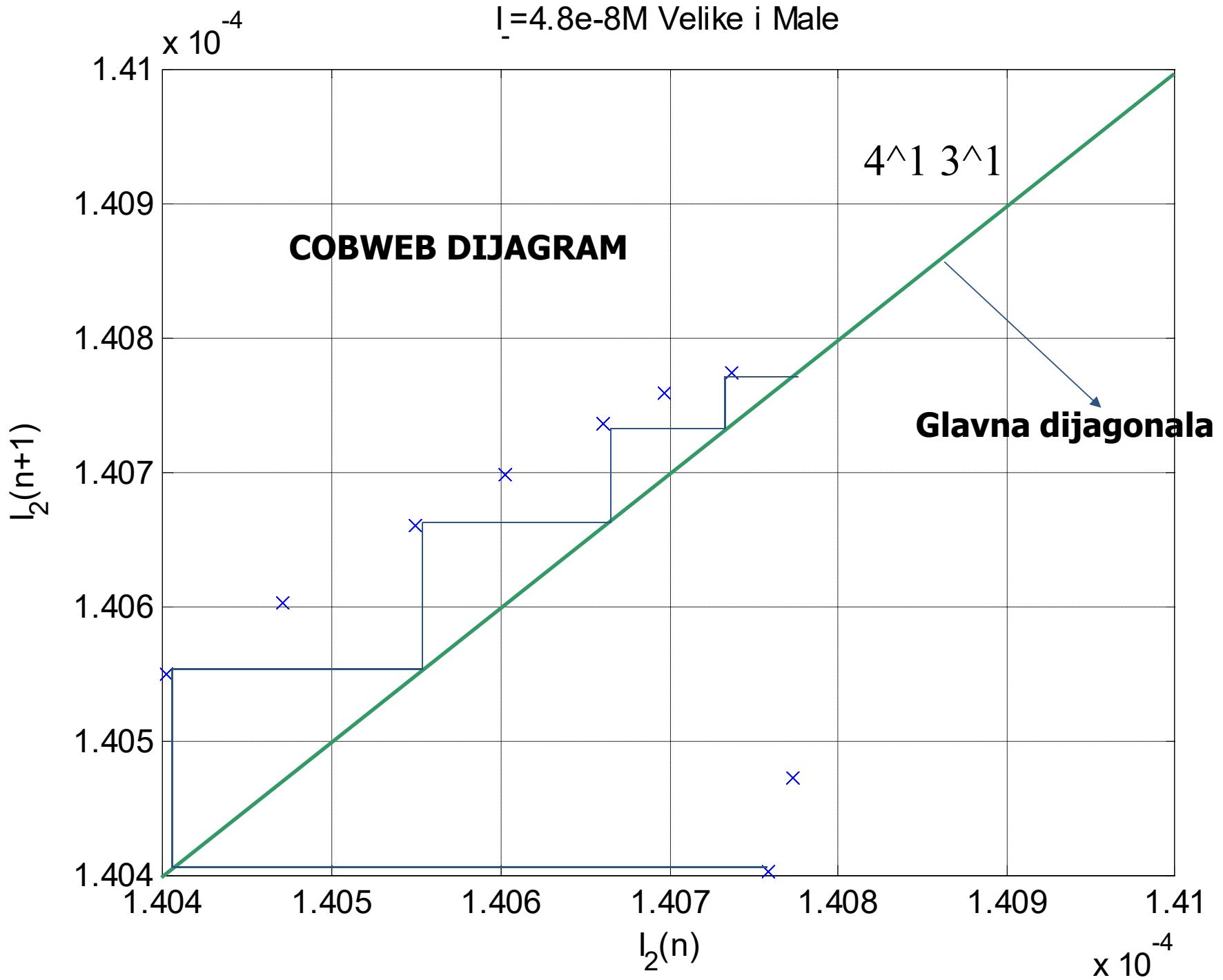


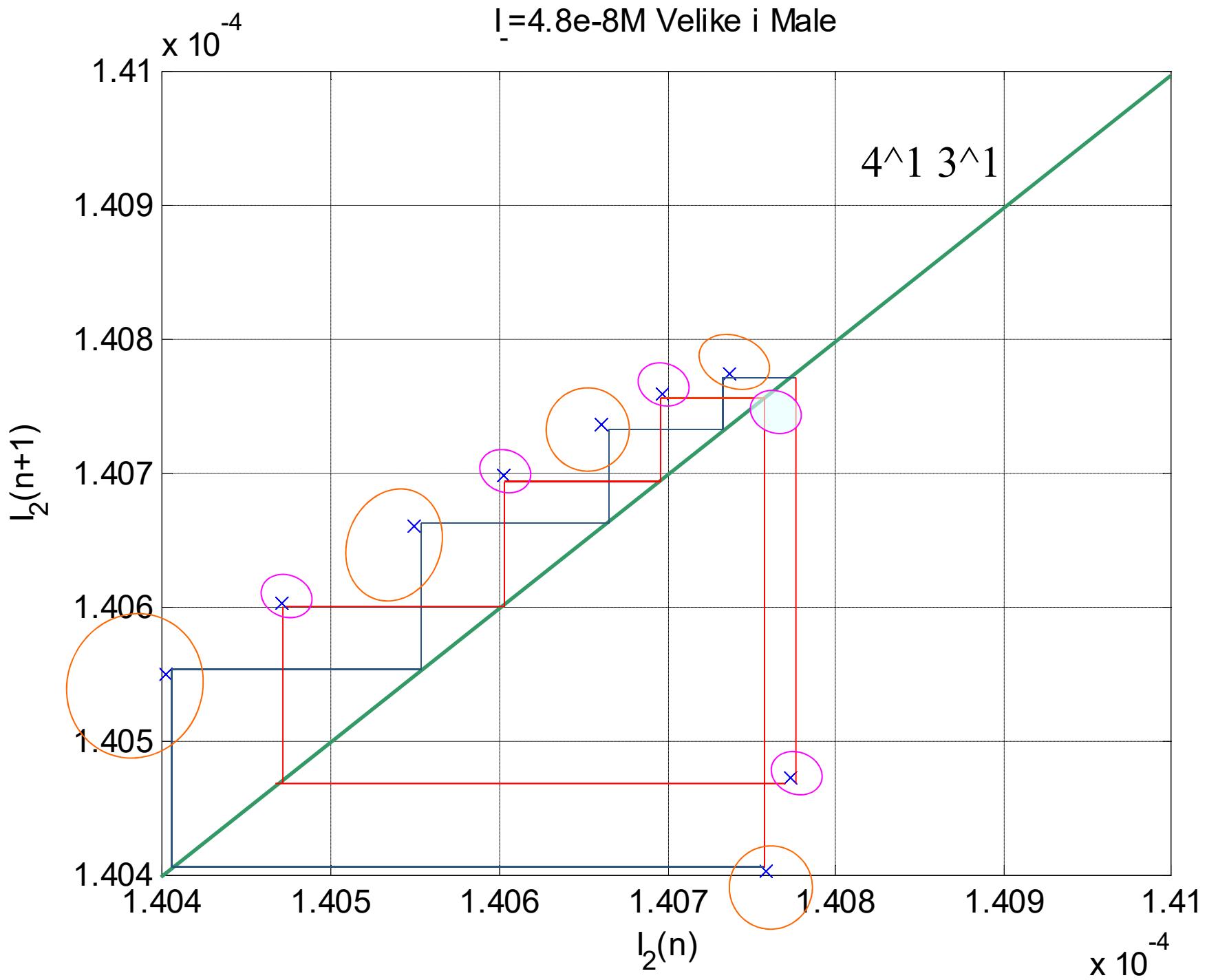


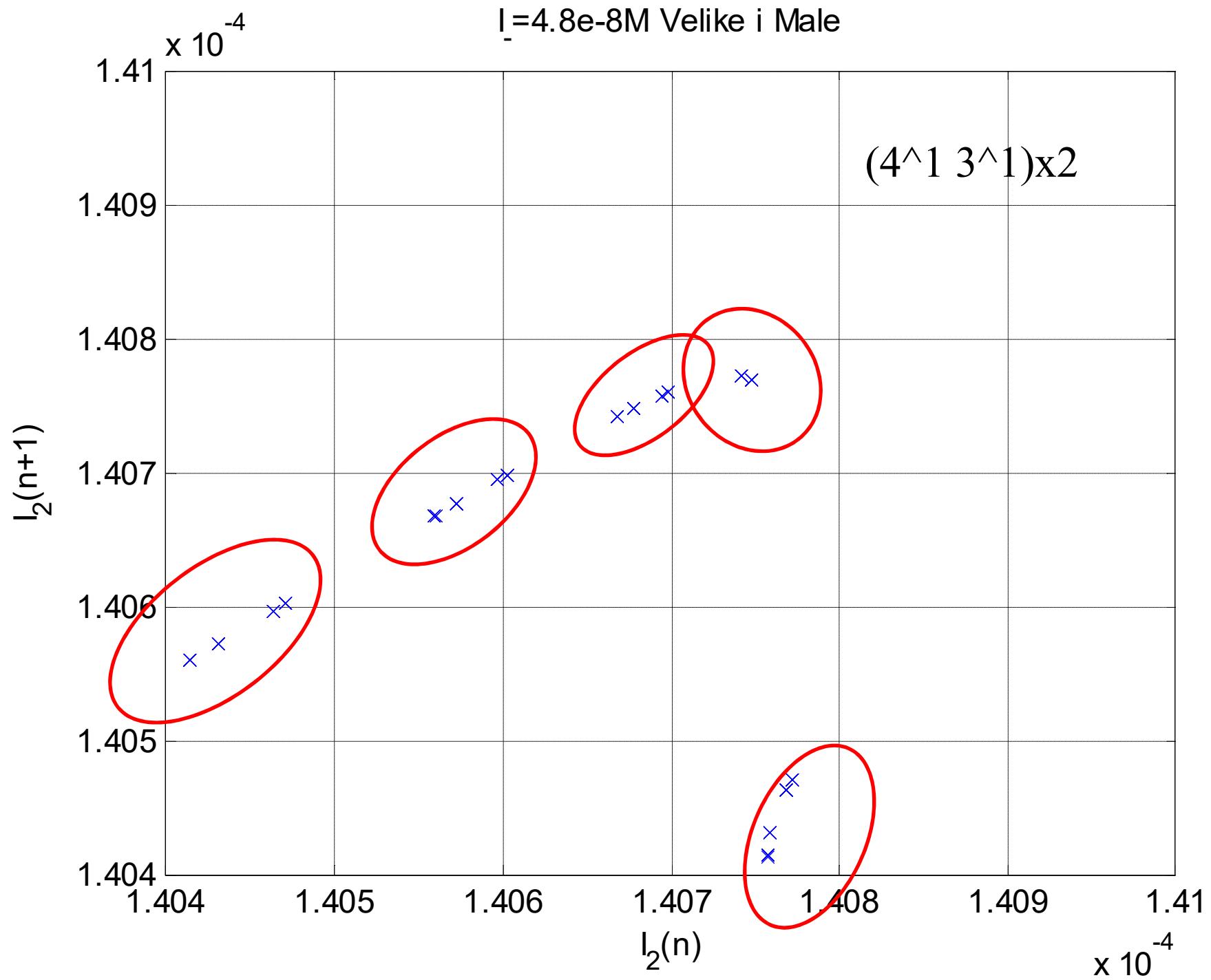


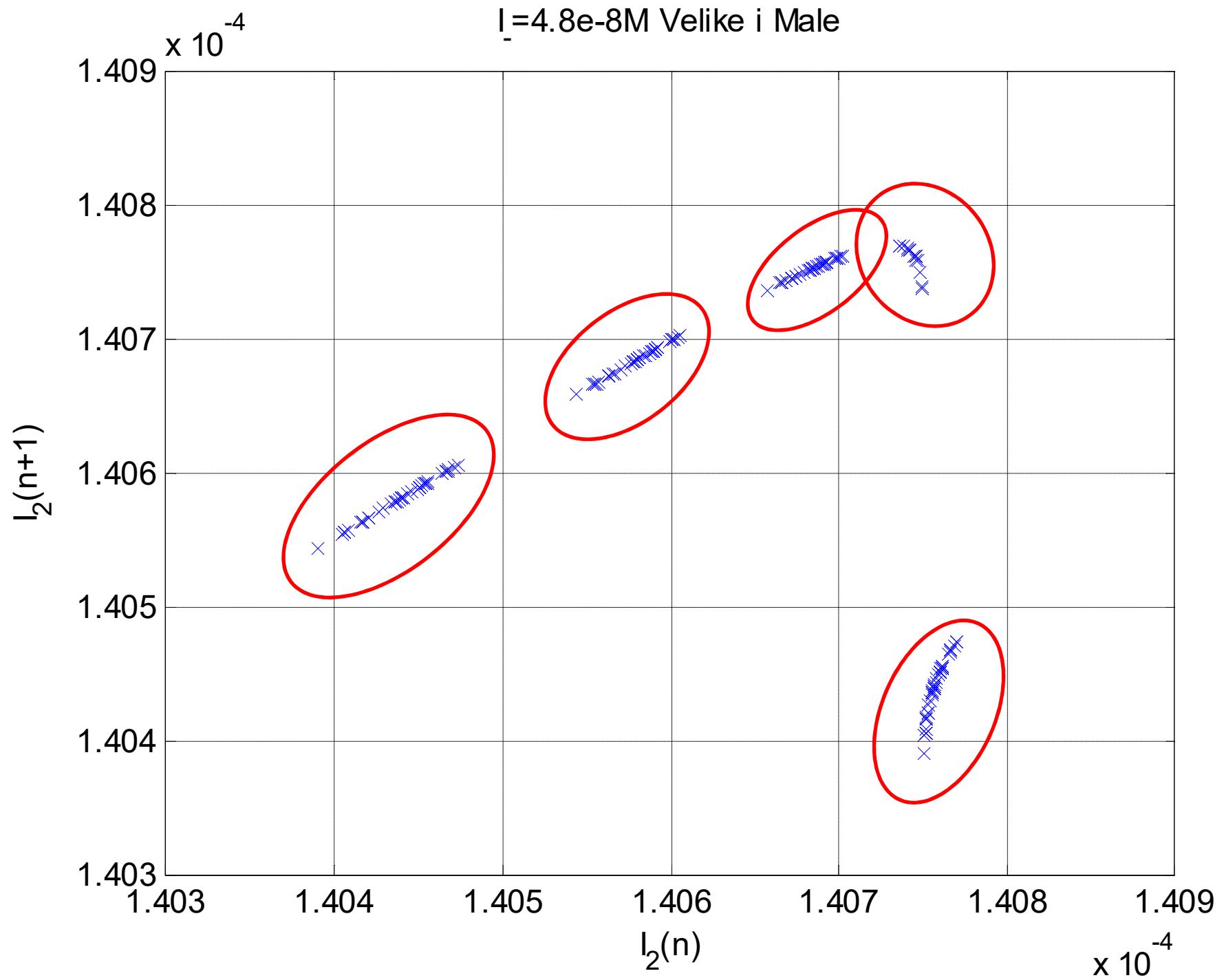


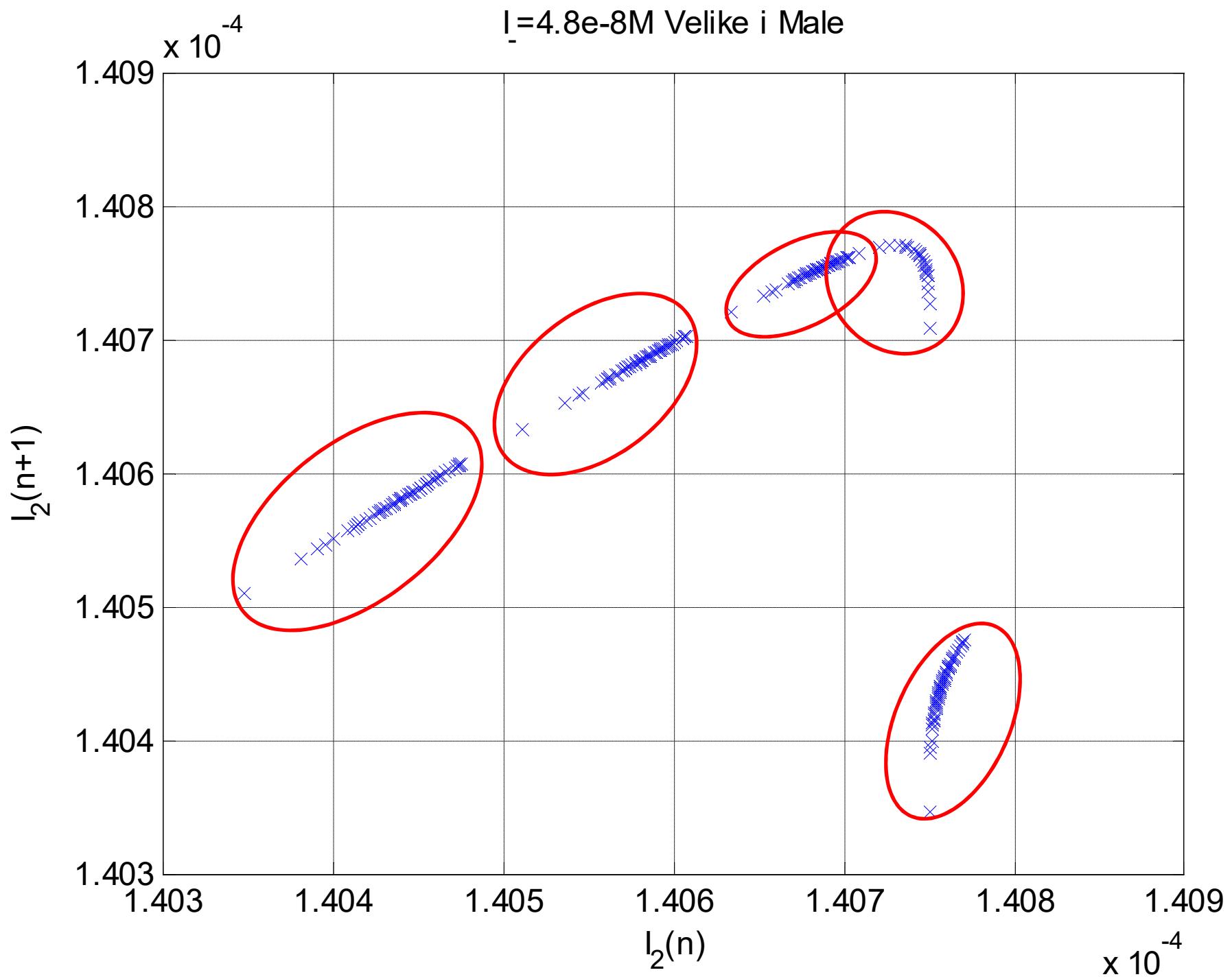


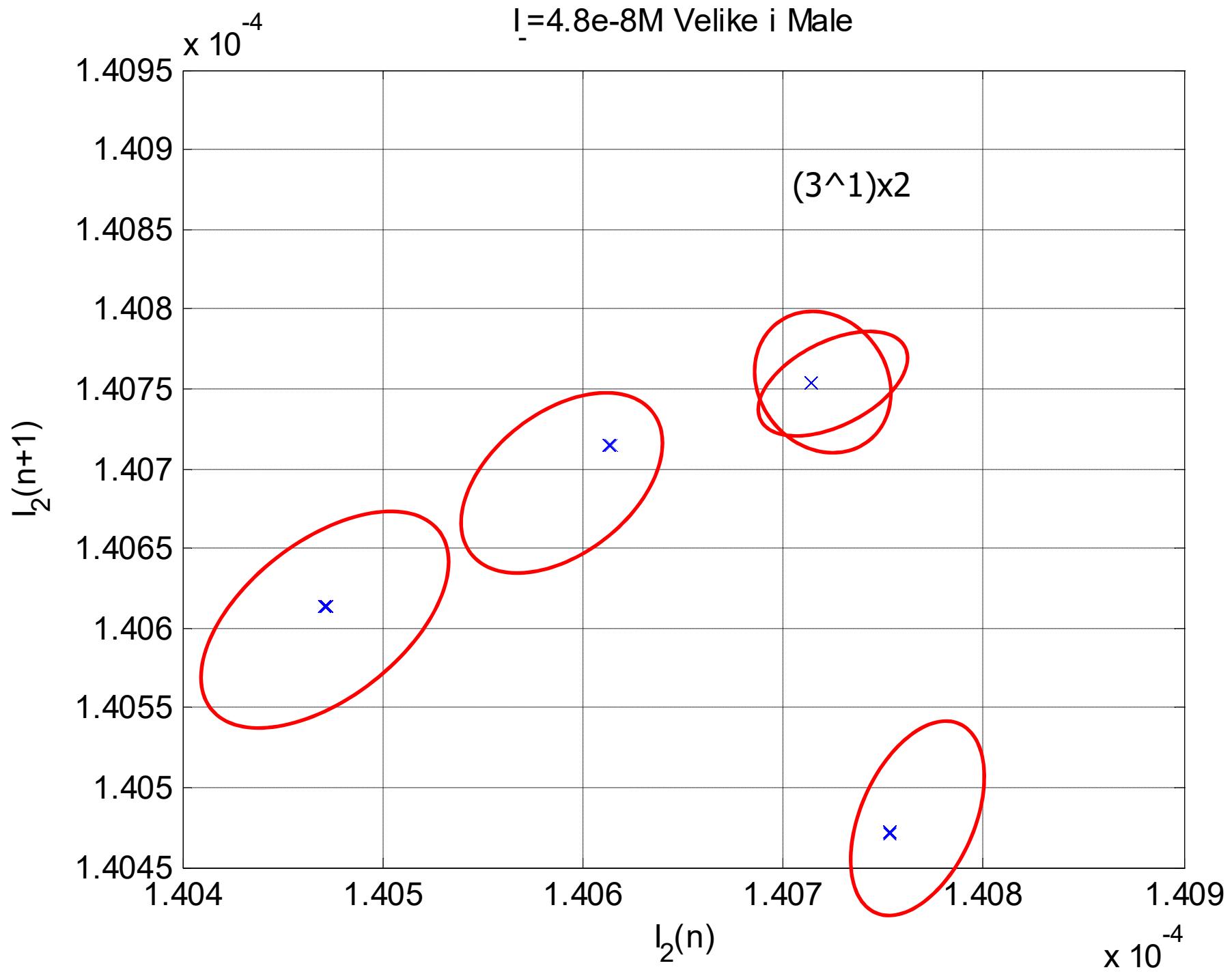


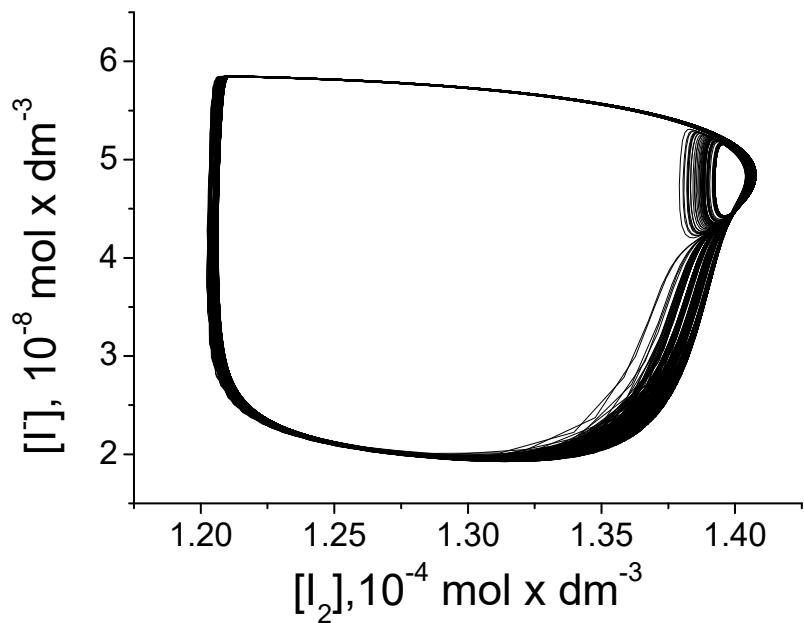








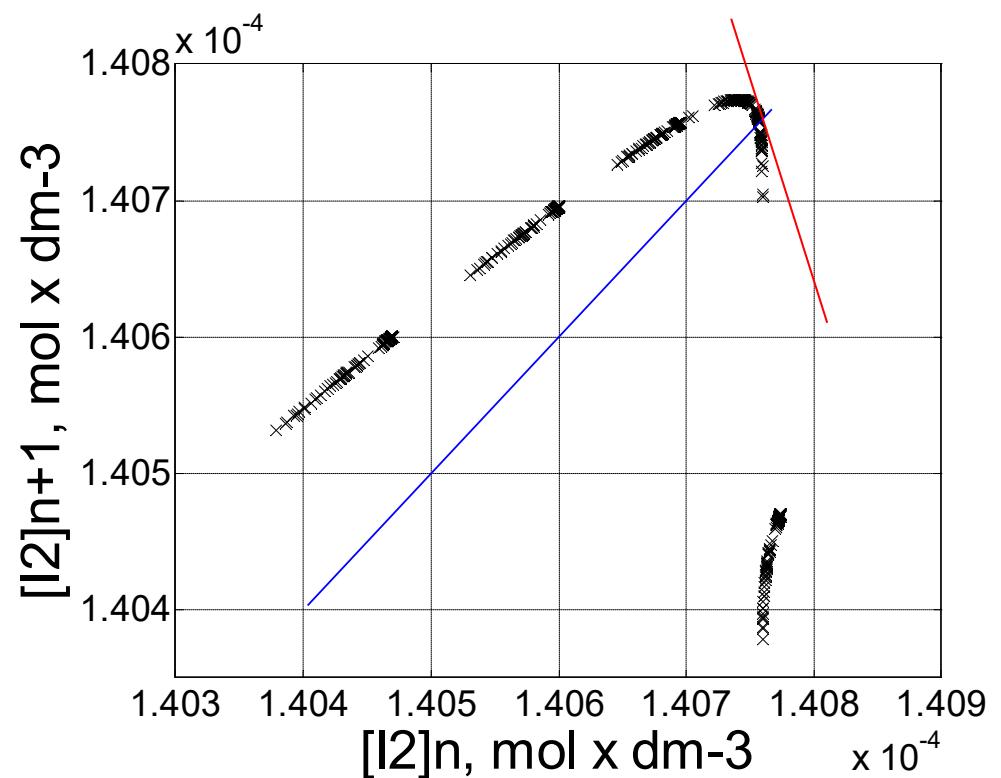




$$x_{n+1}^* = x_n^*$$

Nestabilna
fiksna tačka

FIKSNA TAČKA



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

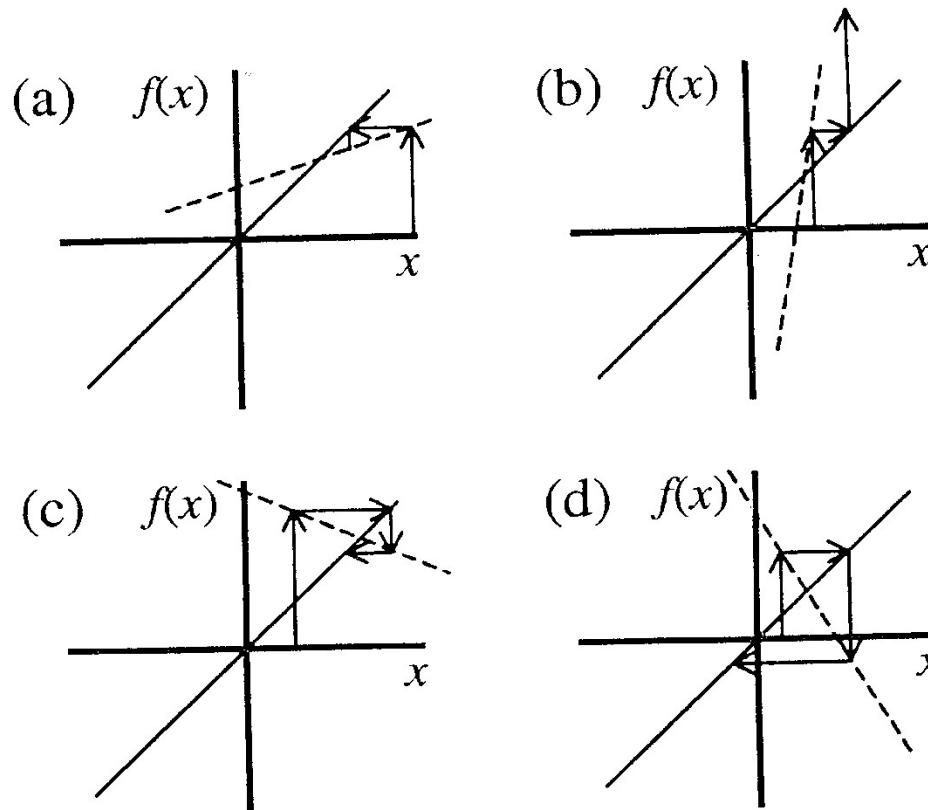


Fig. 5.5. A graphical representation of the effect of repeated use of map function $f(x)$. The map function is plotted as a dashed line. The $f(x) = x$ line is solid. (a) $0 < df/dx < 1$ gives a stable fixed point. (b) $df/dx > 1$ gives an unstable fixed point. (c) $-1 < df/dx < 0$ gives a stable fixed 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.

• G_1, \dots, G_n need a Taylor series expansion near x^* to arrive at the same

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