Simulation of the Belousov-Zhabotinsky Chemical Oscillator using Python

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PHY-150

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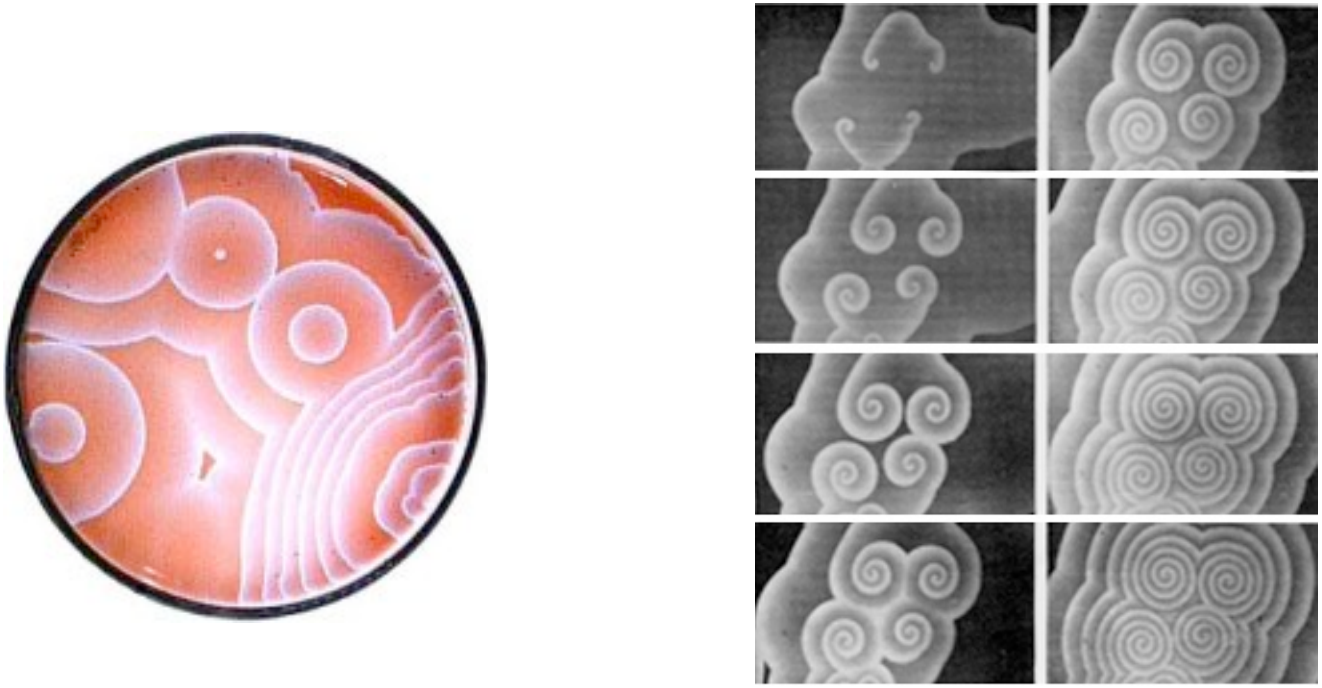
The famous B-Z reaction creates fantastic designs in small dishes



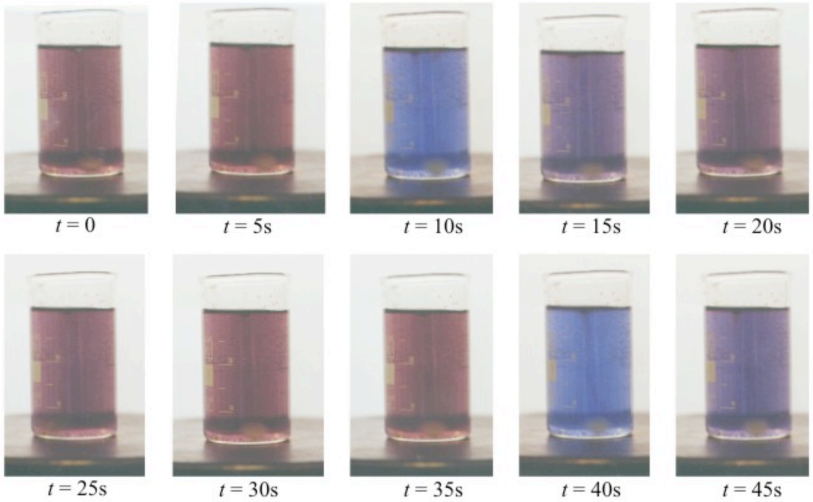
Background:


Belousov


Zhabotinsky

- Originally found by Boris Belousov sometime in the 1950s- could not get the work published initially
- Study was continued in 1961 by Anatol Zhabotinsky

Simple oscillatory behavior like that shown to the right, can last for several hours before equilibrium is reached*



* Scott,S.K. 1992. Chemical Chaos

80-step mechanisms have been proposed

	1. Неорганическая часть				
1	$HOBr + Br^- + H^+ \rightarrow Br_2 + H_2O$	$2.3\cdot10^{9}$	8	$BrO_3^- + HOBr + H^+ \rightarrow 2HBrO_2$	$7.5\cdot10^{-9}$
2	$Br_2 + H_2O \rightarrow HOBr + Br^- + H^+$	2.0	9	$BrO_3^- + HBrO_2 + H^+ \rightarrow Br_2O_4 + H_2O$	33.0
3	$Br^- + HBrO_2 + H^+ \rightarrow 2HOBr$	$2.0\cdot10^{6}$	10	$Br_2O_4 + H_2O \rightarrow BrO_3^- + HBrO_2 + H^+$	2200
4	$2HOBr \rightarrow Br^- + HBrO_2 + H^+$	$2.0\cdot10^{-5}$	11	$Br_2O_4 \rightarrow 2BrO_2^{\bullet}$	$7.4\cdot10^{4}$
5	$Br^- + HBrO_3^- + 2H^+ \rightarrow HOBr + HBrO_2$	2.0	12	$2BrO_2^{\bullet} \rightarrow Br_2O_4$	$1.4\cdot10^{9}$
6	$HOBr + HBrO_2 \rightarrow Br^- + HBrO_3^- + 2H^+$	3.3	13	$Ce^{3+} + 2BrO_2^{\bullet} + H^+ \rightarrow HBrO_2 + Ce^{4+}$	$5.2\cdot10^{4}$
7	$2HBrO_2 \rightarrow BrO_3^- + HOBr + H^+$	$3.0\cdot10^{3}$	14	$HBrO_2 + Ce^{4+} \rightarrow Ce^{3+} + 2BrO_2^{\bullet} + H^+$	$7.0\cdot10^{3}$
	2. Реакции с участием органических веществ				
	а) Реакции без участия и образования радикалов				
15	$MA \rightarrow ENOL$	$3.0\cdot10^{-3}$	20	$TTA + HOBr \rightarrow BrTTA + H_2O$	5.0
16	$ENOL \rightarrow MA$	200.0	21	$BrO_2MA + H_2O \rightarrow HBrO_2 + TTA$	1.0
17	$ENOL + Br_2 \rightarrow BrMA + Br^- + H^+$	$1.91\cdot10^{6}$	22	$BrO_2MA \rightarrow HOBr + MOA$	1.0
18	$MA + HOBr \rightarrow Br_2MA + H_2O$	8.2	23	$BrO_2TTA \rightarrow HBrO_2 + MOA$	1.0
19	$Br_2MA + H_2O \rightarrow MA + HOBr$	0.1	24	$BrTTA \rightarrow Br^- + MOA + H^+$	1.0
	б) Реакции с образованием радикалов				
25	$Ce^{4+} + BrMA \rightarrow Ce^{3+} + BrMA^{\bullet} + H^+$	0.09	29	$Ce^{4+} + MOA + H_2O \rightarrow Ce^{3+} + OA + {}^{\bullet}COOH + H^+$	10.0
26	$Ce^{4+} + MA \rightarrow Ce^{3+} + MA^{\bullet} + H^+$	0.23	30	$HOBr + OA \rightarrow Br^{\bullet} + {}^{\bullet}COOH + CO_2 + H_2O$	140.0
27	$Ce^{4+} + TTA \rightarrow Ce^{3+} + TTA^{\bullet} + H^+$	0.66	31	$Ce^{4+} + OA \rightarrow Ce^{3+} + {}^{\bullet}COOH + H^+ + CO_2 + H^+$	10.0
28	$HOBr + MOA \rightarrow Br^{\bullet} + OA + {}^{\bullet}COOH$	140.0	32	$BrO_3^- + OA + H^+ \rightarrow BrO_2^{\bullet} + {}^{\bullet}COOH + CO_2 + H^+$	$1.6\cdot10^{-5}$
	в) Реакции гибели радикалов				
33	$2Br^{\bullet} \rightarrow Br_2$	$1.0\cdot10^{8}$	44	$MA^{\bullet} + Br^{\bullet} \rightarrow BrMA$	$1.0\cdot10^{9}$
34	$Br^{\bullet} + BrMA^{\bullet} \rightarrow Br_2MA$	$1.0\cdot10^{9}$	45	$MA^{\bullet} + Ce^{3+} + H^+ \rightarrow MA + Ce^{4+}$	$1.7\cdot10^{4}$
35	$2BrMA^{\bullet} + H_2O \rightarrow BrMA + BrTTA$	$1.0\cdot10^{8}$	46	$MA^{\bullet} + BrO_2^{\bullet} \rightarrow BrO_2MA$	$5.0\cdot10^{9}$
36	$BrMA^{\bullet} + MA + H_2O \rightarrow MA + BrTTA$	$1.0\cdot10^{9}$	47	$2TTA^{\bullet} \rightarrow TTA + MOA$	$1.0\cdot10^{9}$
37	$BrMA^{\bullet} + TTA^{\bullet} + H_2O \rightarrow TTA + BrTTA$	$1.0\cdot10^{9}$	48	$TTA^{\bullet} + {}^{\bullet}COOH \rightarrow TTA + CO_2$	$2.0\cdot10^{9}$
38	$BrMA^{\bullet} + Ce^{4+} + H_2O \rightarrow Ce^{3+} + BrTTA + H^+$	$1.0\cdot10^{7}$	49	$TTA^{\bullet} + Br^{\bullet} \rightarrow BrTTA$	$1.0\cdot10^{9}$
39	$BrMA^{\bullet} + BrO_2^{\bullet} + H_2O \rightarrow HBrO_2 + BrTTA$	$5.0\cdot10^{9}$	50	$TTA^{\bullet} + Ce^{3+} + H^+ \rightarrow TTA + Ce^{4+}$	$1.7\cdot10^{4}$
40	$BrMA^{\bullet} + {}^{\bullet}COOH \rightarrow BrMA + CO_2$	$5.0\cdot10^{8}$	51	$TTA^{\bullet} + BrO_2^{\bullet} \rightarrow BrO_2TTA$	$5.0\cdot10^{9}$
41	$2MA^{\bullet} + H_2O \rightarrow MA + TTA$	$3.2\cdot10^{9}$	52	$2{}^{\bullet}COOH \rightarrow OA$	$1.2\cdot10^{9}$
42	$MA^{\bullet} + TTA^{\bullet} + H_2O \rightarrow 2TTA$	$1.0\cdot10^{9}$	53	${}^{\bullet}COOH + Ce^{4} \rightarrow Ce^{3+} + CO_2 + H^+$	$1.0\cdot10^{7}$
43	$MA^{\bullet} + {}^{\bullet}COOH \rightarrow MA + CO_2$	$2.0\cdot10^{9}$	54	${}^{\bullet}COOH + Br^{\bullet} \rightarrow Br^- + CO_2 + H^+$	$1.0\cdot10^{9}$
			55	${}^{\bullet}COOH + BrO_2^{\bullet} \rightarrow HBrO_2 + CO_2$	$5.0\cdot10^{9}$
	г) Реакции продолжения цепи				
56	$MA^{\bullet} + Br_2 \rightarrow BrMA + Br^{\bullet}$	$1.5\cdot10^{8}$	69	$BrMA^{\bullet} + HOBr \rightarrow BrTTA + Br^{\bullet}$	$1.0\cdot10^{5}$
57	$MA^{\bullet} + HOBr \rightarrow TTA + Br^{\bullet}$	$1.0\cdot10^{7}$	70	$BrMA^{\bullet} + BrO_3^- + H^+ \rightarrow BrTTA + BrO_2^{\bullet}$	40.0
58	$MA^{\bullet} + BrO_3^- + H^+ \rightarrow TTA + BrO_2^{\bullet}$	40.0	71	${}^{\bullet}COOH + BrMA \rightarrow Br^- + MA^{\bullet} + CO_2 + H^+$	$1.0\cdot10^{7}$
59	$MA^{\bullet} + TTA \rightarrow MA + TTA$	$1.0\cdot10^{5}$	72	${}^{\bullet}COOH + Br_2 \rightarrow Br^- + Br^{\bullet} + CO_2 + H^+$	$1.5\cdot10^{8}$
60	$TTA^{\bullet} + MA \rightarrow MA^{\bullet} + TTA$	$1.0\cdot10^{5}$	73	${}^{\bullet}COOH + HOBr \rightarrow Br^{\bullet} + CO_2 + H_2O$	$2.0\cdot10^{7}$
61	$MA^{\bullet} + BrMA \rightarrow MA + BrMA^{\bullet}$	$1.0\cdot10^{5}$	74	${}^{\bullet}COOH + BrO_3^- + H^+ \rightarrow BrO_2^{\bullet} + CO_2 + H_2O$	$2.1\cdot10^{3}$
62	$BrMA^{\bullet} + MA \rightarrow BrMA + MA^{\bullet}$	$5.0\cdot10^{2}$	75	$Br^{\bullet} + MA \rightarrow Br^- + MA^{\bullet} + H^+$	$1.0\cdot10^{5}$
63	$TTA^{\bullet} + BrMA \rightarrow TTA + BrMA^{\bullet}$	$2.0\cdot10^{5}$	76	$Br^{\bullet} + TTA \rightarrow Br^- + TTA^{\bullet} + H^+$	$1.0\cdot10^{6}$
64	$BrMA^{\bullet} + TTA \rightarrow BrMA + TTA^{\bullet}$	$5.0\cdot10^{3}$	77	$Br^{\bullet} + BrMA \rightarrow Br^- + BrMA^{\bullet} + H^+$	$5.0\cdot10^{6}$
65	$TTA^{\bullet} + Br_2 \rightarrow BrTTA + Br^{\bullet}$	$1.0\cdot10^{8}$	78	$Br^{\bullet} + MOA + H_2O \rightarrow Br^- + OA + {}^{\bullet}COOH + H^+$	$2.0\cdot10^{3}$
66	$TTA^{\bullet} + HOBr \rightarrow MOA + Br^{\bullet} + H_2O$	$1.0\cdot10^{7}$	79	$Br^{\bullet} + OA \rightarrow Br^- + {}^{\bullet}COOH + CO_2 + H^+$	$2.0\cdot10^{3}$
67	$TTA^{\bullet} + BrO_3^- + H^+ \rightarrow MOA + BrO_2^{\bullet} + H_2O$	40.0	80	$BrO_2^{\bullet} + OA \rightarrow HBeO_2 + {}^{\bullet}COOH + CO_2$	$1.0\cdot10^{2}$
68	$BrMA^{\bullet} + Br_2 \rightarrow Br_2MA + Br^{\bullet}$	$1.0\cdot10^{6}$			

Moral of the story:
The chemistry details are extremely complicated

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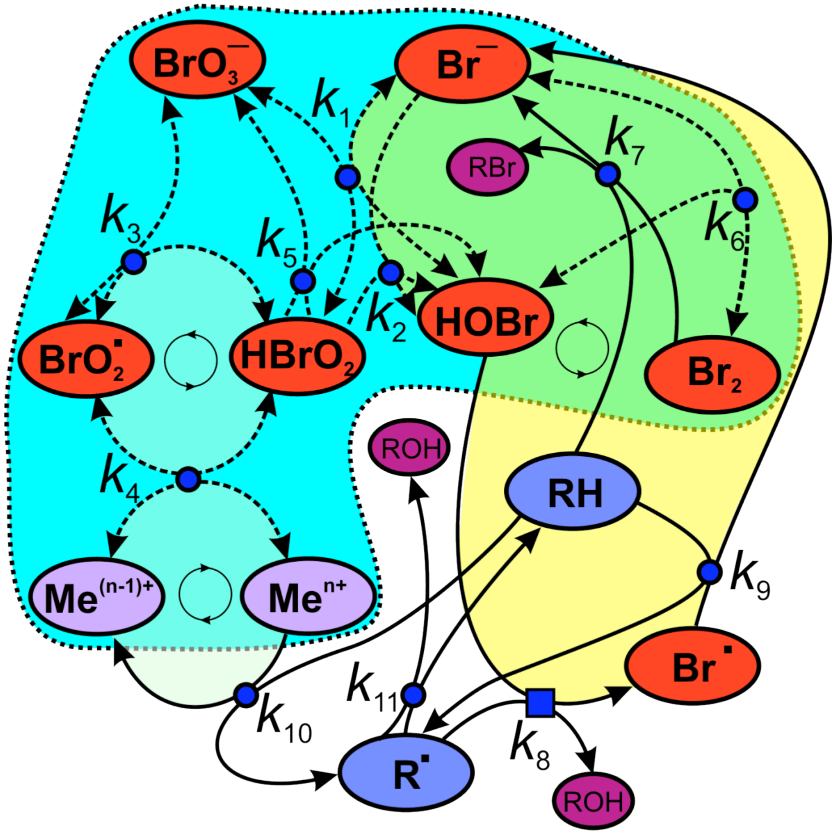
Simpler mechanisms are better for modeling: here, an 11-step mechanism



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ODEs: the “Oregonator”

Field-Noyes Version:

$$dX/dt = k_3AY - k_2XY + k_5BX - 2k_4X^2$$

$$dY/dt = -k_3AY - k_2XY + f\, k_j\, Z$$

$$dZ/dt = 2k_5BX - k_jZ$$

$A = B \equiv [BrO3^-]$

$X \equiv [HBrO_2]$

$Y \equiv [Br^-]$

$Z \equiv [Ce^{4+}]$

All rate constants estimated from empirical experiments

Field and Noyes. 1974. Oscillations in chemical systems.

Tyson's Version

- Convenient non-dimensionalization
- Simplest three-variable BZ model

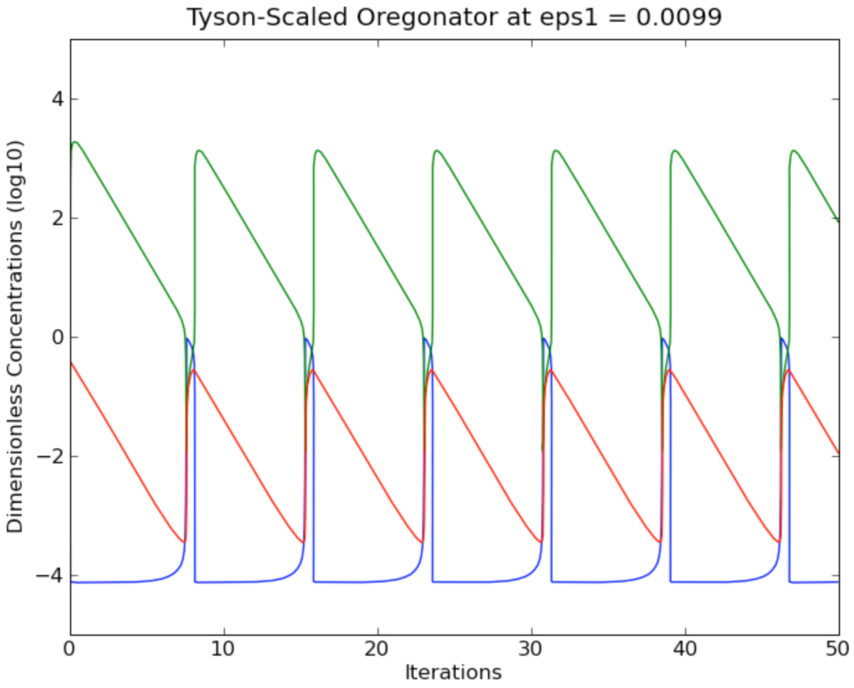
$$dx/dt = (qy - xy + x(1-x))/\varepsilon$$

$$dy/dt = (-qy - xy + fz)/\varepsilon'$$

$$dz/dt = x - z$$

J.J. Tyson, 1985
Oscillations and Traveling Waves in Chemical Systems
Edited by Field & Burger pp. 111-112

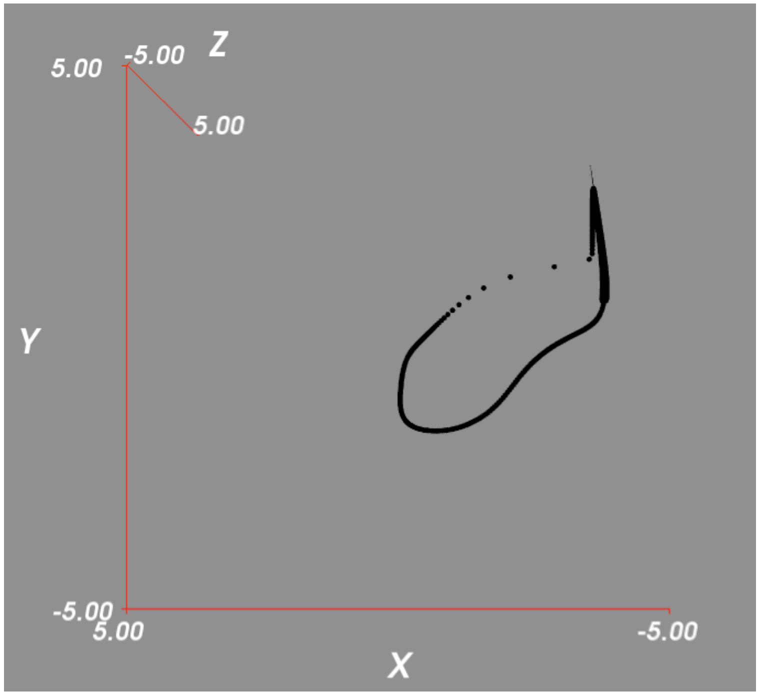
Limit cycles, but no chaos



Green = $\log_{10}$(scaled Ce^{4+})

Red = $\log_{10}$(scaled Br^{-})

Blue = $\log_{10}$(scaled HBrO_2)



Corresponding 3D Attractor

* 2D Plot made by matplotlib
* 3D Plot made by MayaVi
* Enthought Python Distribution

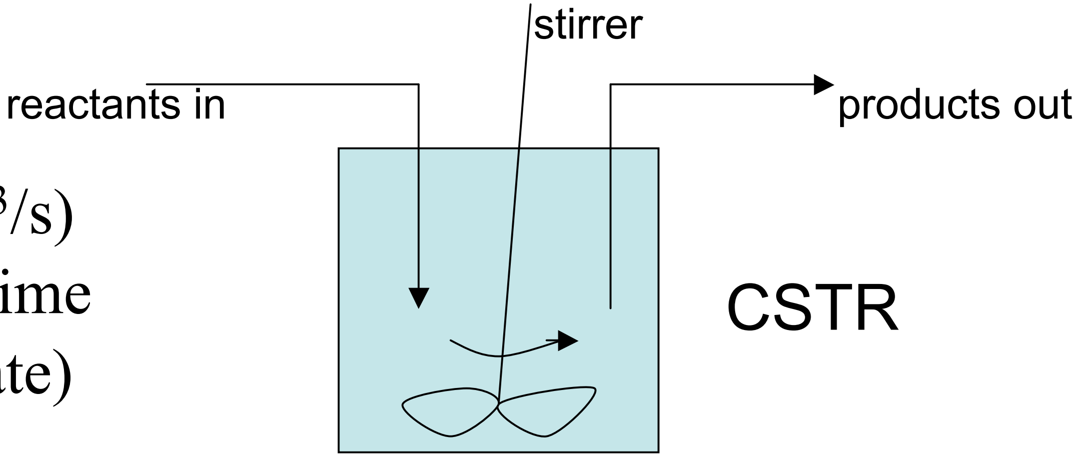
Continuous-flow Stirred Tank Reactors (CSTR)

- Avoids equilibrium by using an open system
- Chaos results from interactions from two frequencies on different timescales*
- frequency1: BZ limit cycle
- frequency2: BrMA cycling concentration

τ = volume (m^3)/flowrate (m^3/s)

$k_f = 1/\tau$ = inverse residence time

(similar to flowrate)



CSTR

*Gyorgyi & Field, 1992 Nature 355 pp. 808-810

7-step mechanism

(1) Y + X + H -> 2 V
(2) Y + A + 2H -> V + X
(3) 2X -> V
(4) 0.5X + A +H -> X + Z
(5) X + Z -> 0.5X
(6) V + Z -> Y
(7) Z + M ->

$Y \equiv Br^-$
$X \equiv HBrO_2$
$Z \equiv Ce(IV)$
$V \equiv BrCH(COOH)_2$
$A \equiv BrO_3^-$
$H \equiv H^+$
$M \equiv CH_2(COOH)_2$

Gyorgyi & Field, 1992 Nature 355 pp. 808-810

chaotic three-variable model based on a 7-parameter rate equation

* k_f term represents the inverse residence time in a CSTR

Scaled Differential Equations:

$$dx/dt = To\{-k_1HY_oxy + k_2AH^2Y_o/X_oy - 2k_3X_ox^2 \\ + 0.5k_4A^{0.5}H^{1.5}X_o - 0.5(C - Z_oz)x^{0.5} \\ - 0.5k_5Z_oxz - \mathbf{k_f}x\}$$

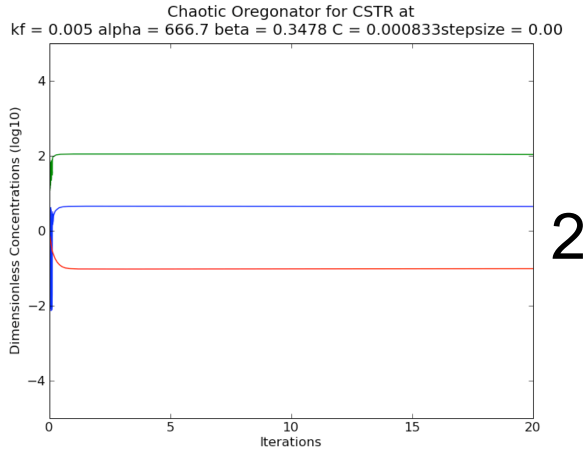
$$dz/dt = To\{k_4A^{0.5}H^{1.5}X^{0.5}(C/Z_o - z)x^{0.5} - k_5X_oxz \\ - \alpha k_6V_ozv - \beta k_7Mz - \mathbf{k_f}z\}$$

$$dv/dt = To\{2k_1HX_oY_o/V_oxy + k_2AH^2Y_o/V_oy \\ + k_3X_o{}^2/V_ox^2 - \alpha k_6Z_ozv - \mathbf{k_f}z$$

Gyorgyi & Field, 1992 Nature 355 pp. 808-810

Period Doubling to Chaos

1



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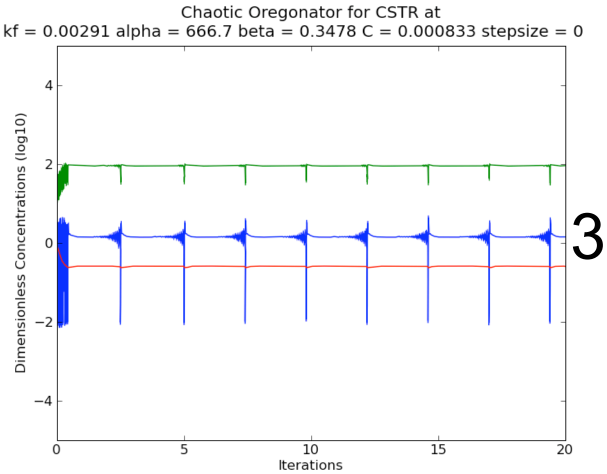

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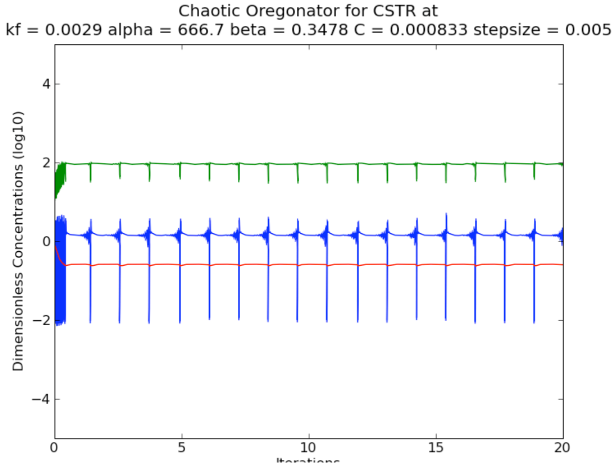

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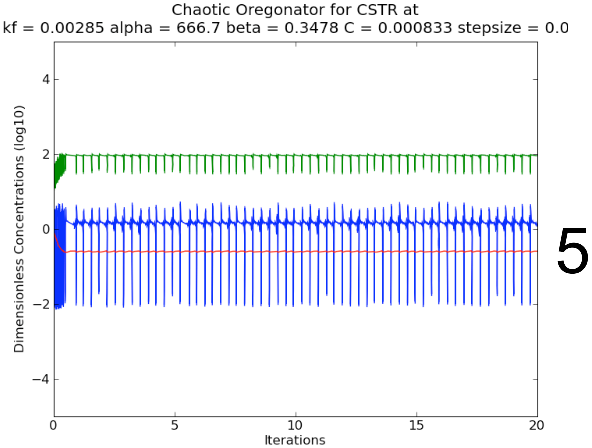

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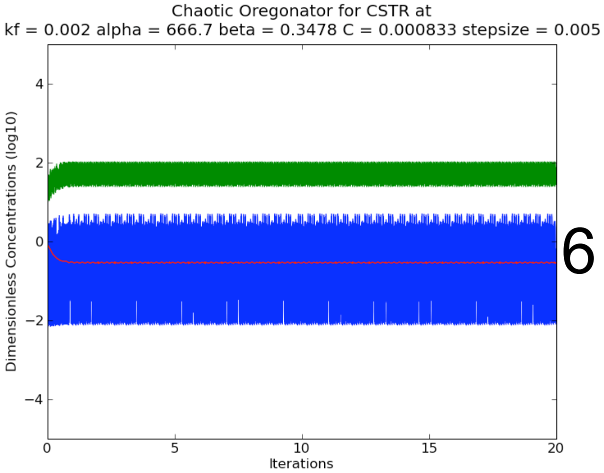

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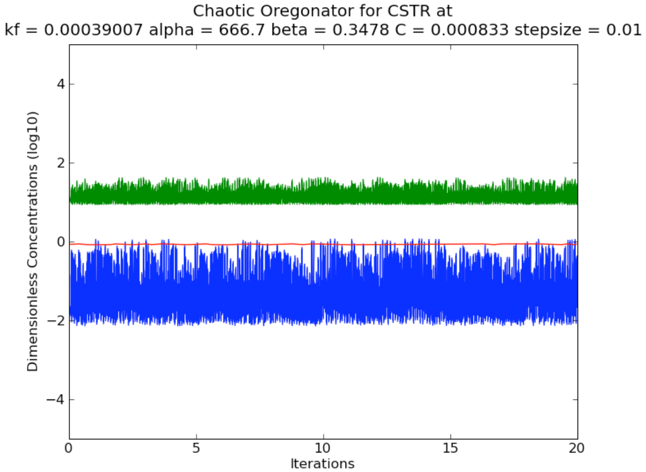
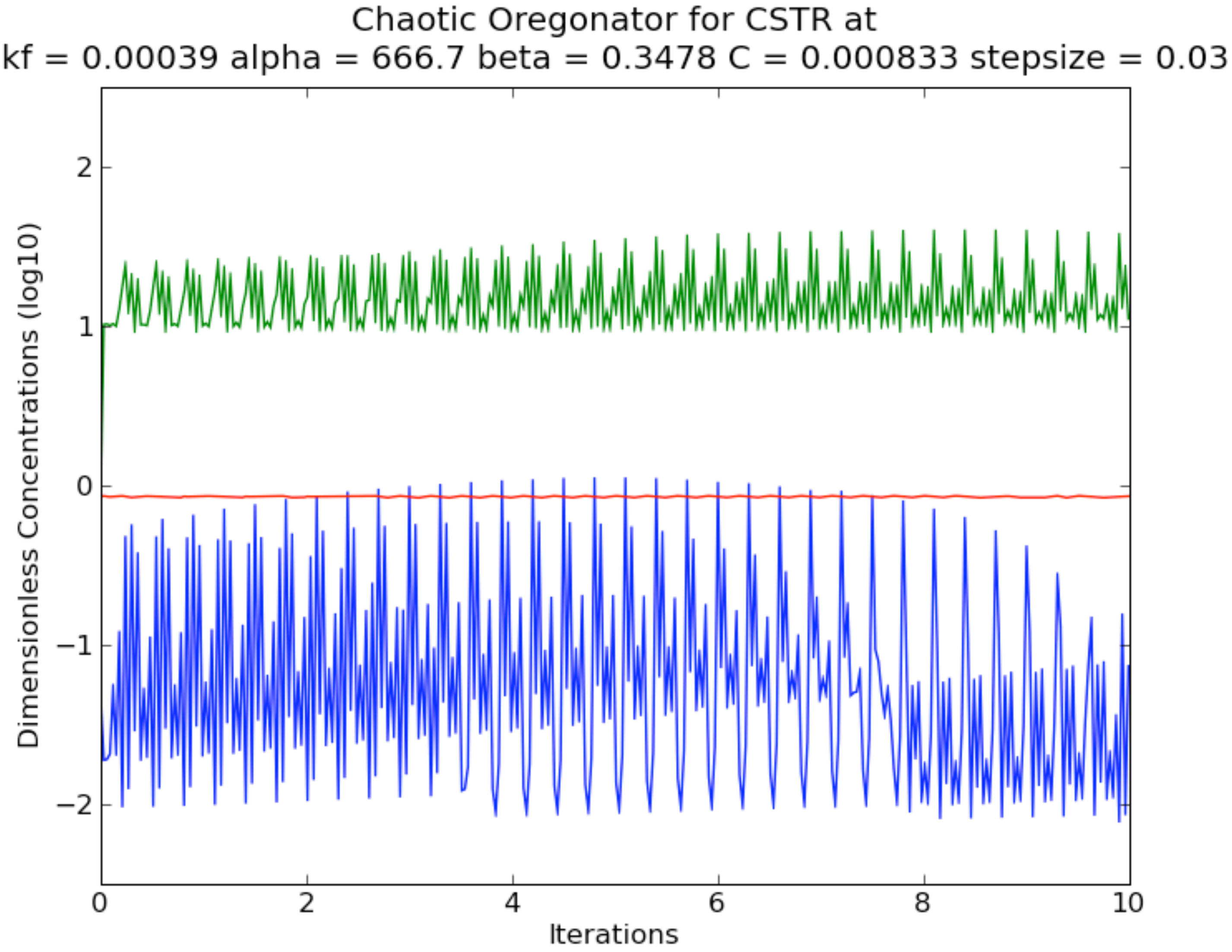
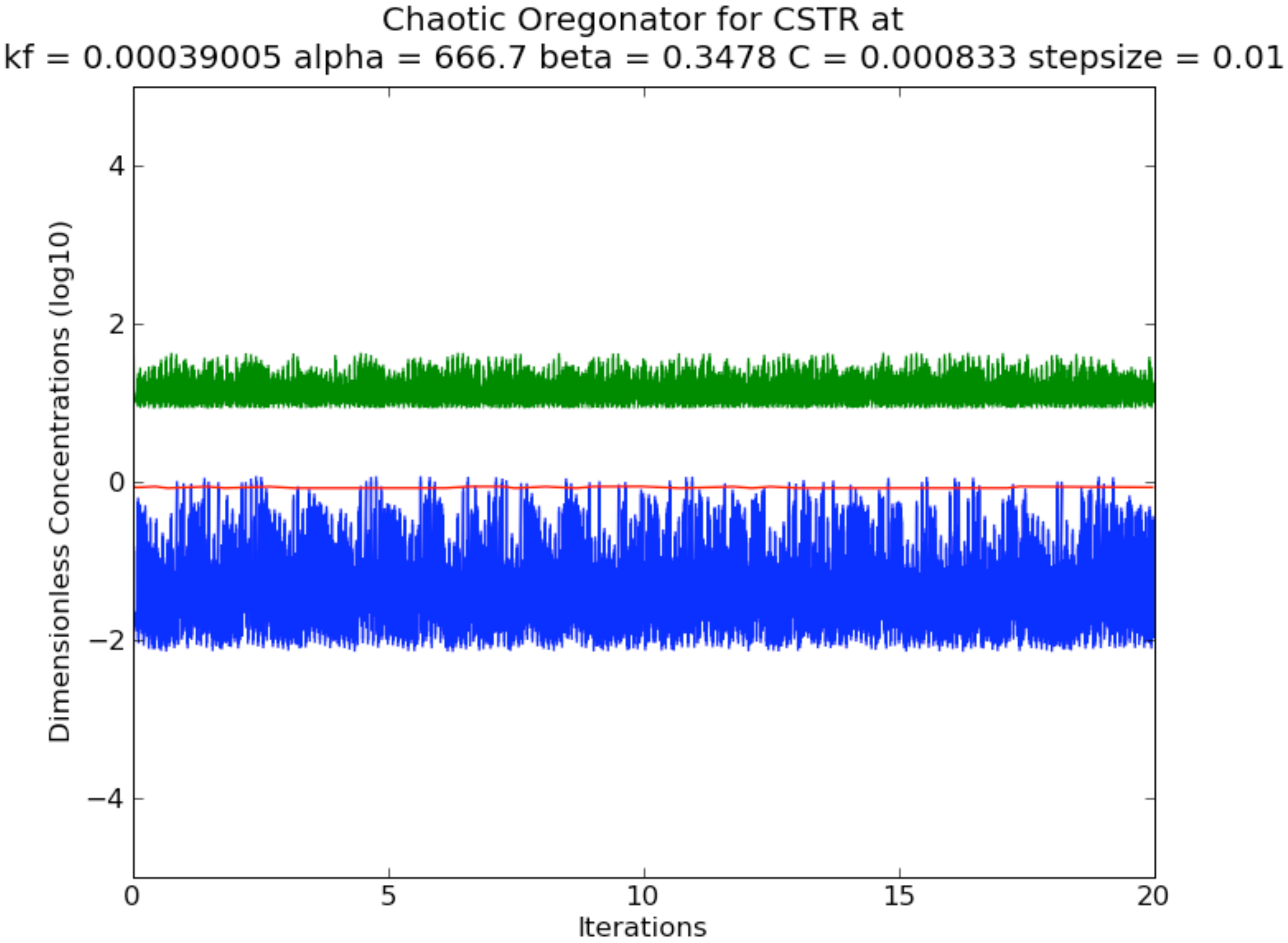
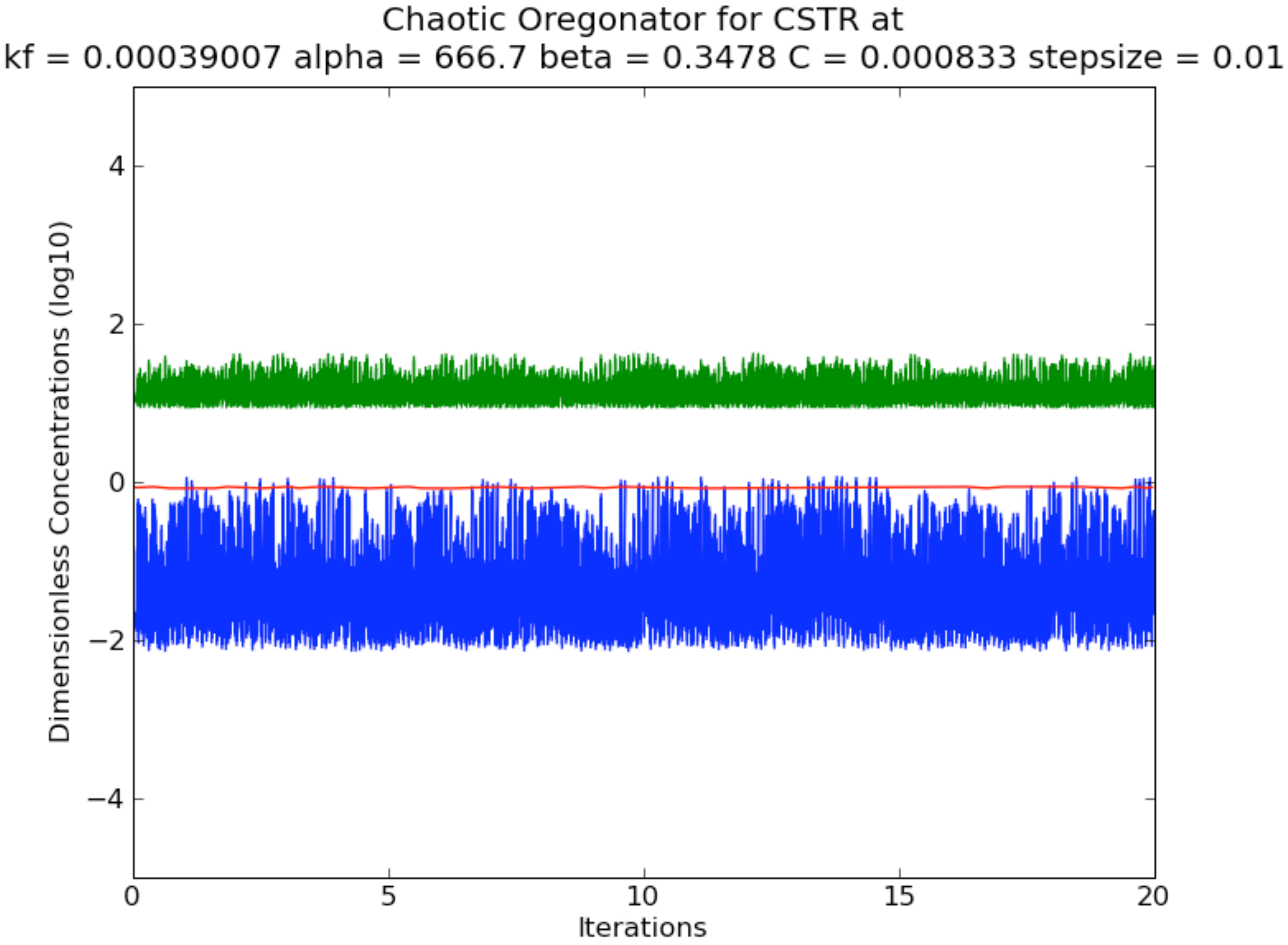


Decreasing flow rate parameter k_f →



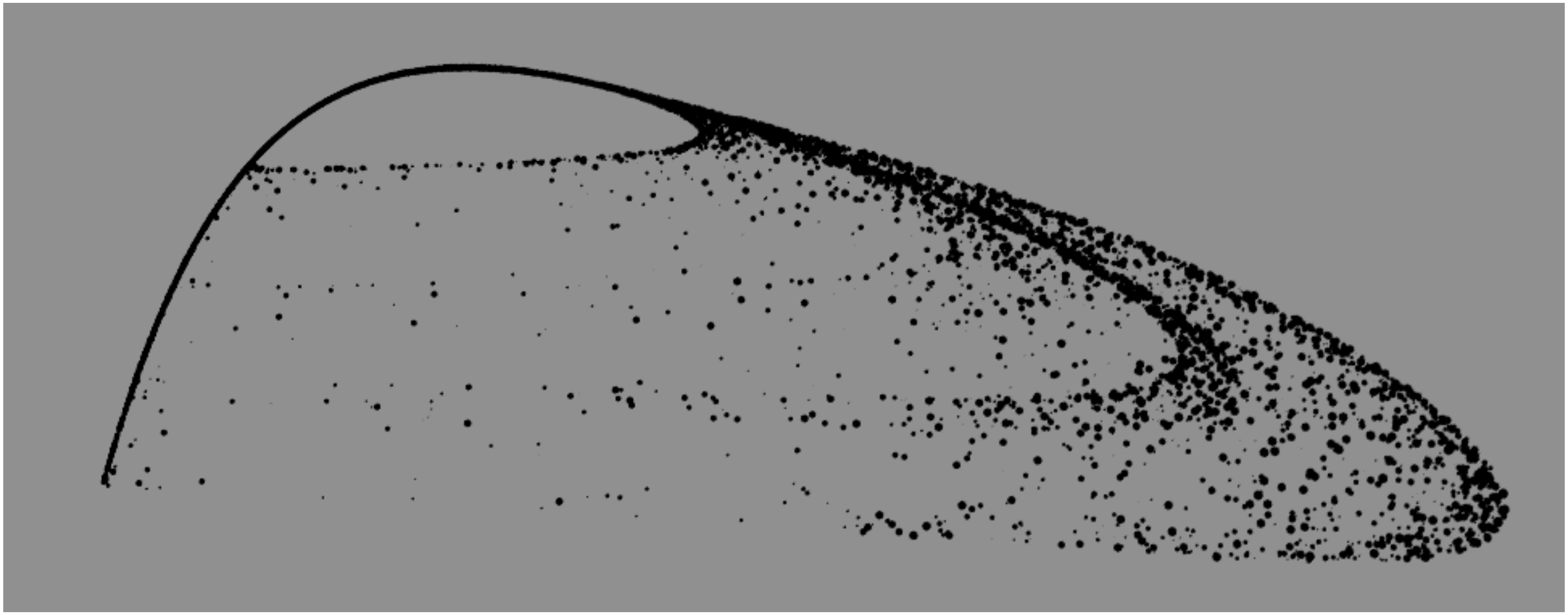
Chaotic Oregonator for CSTR at
kf = 0.00039 alpha = 666.7 beta = 0.3478 C = 0.000833 stepsize = 0.03


Chaotic Oregonator for CSTR at
kf = 0.00039005 alpha = 666.7 beta = 0.3478 C = 0.000833 stepsize = 0.01
Dimensionless Concentrations (log10)
4
2
0
−2
−4
0
5
10
15
20
Iterations



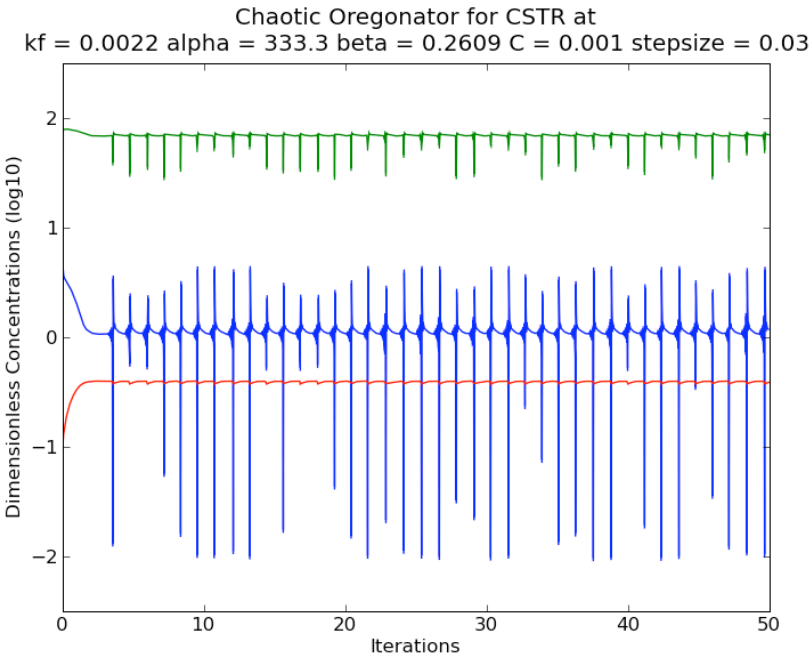
Chaotic Oregonator for CSTR at
kf = 0.00039007 alpha = 666.7 beta = 0.3478 C = 0.000833 stepsize = 0.01

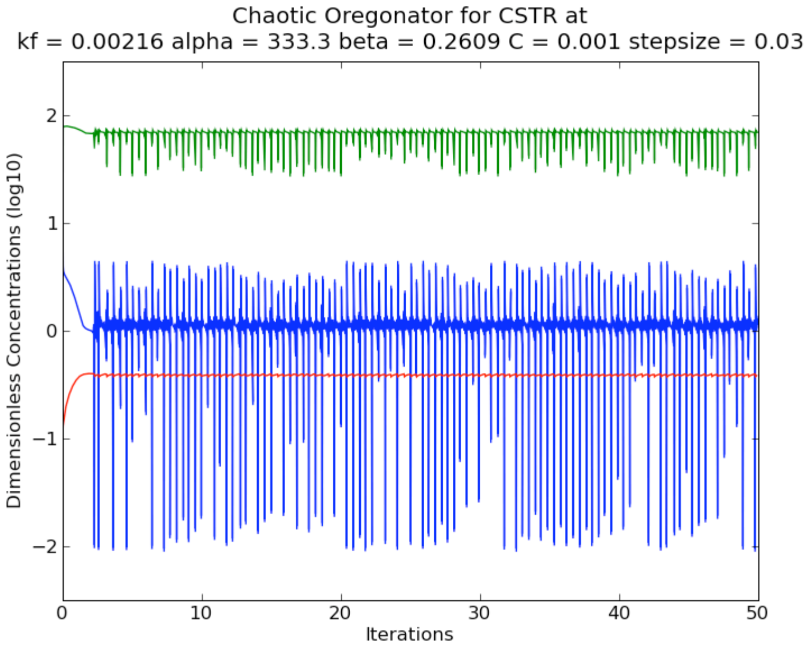
attractor formed at low ‘flowrate’ conditions



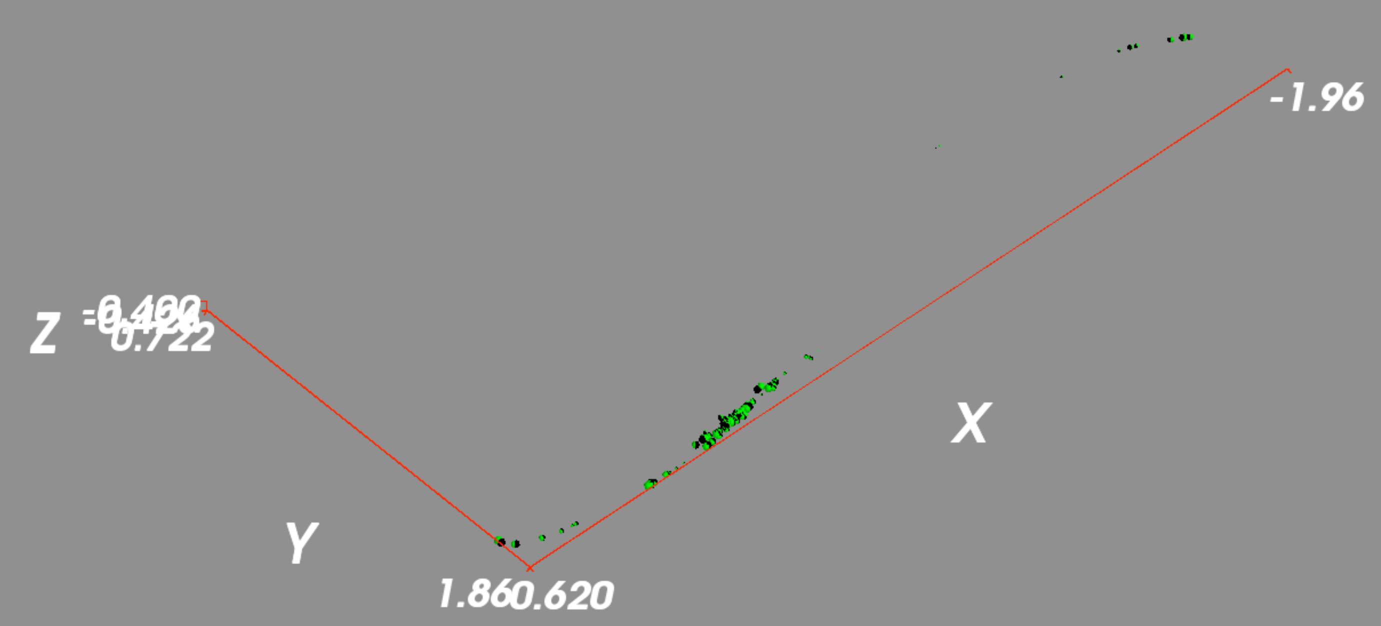
the attractor is virtually 2D

Higher Flow Rate Conditions





sensitive dependence on initial conditions

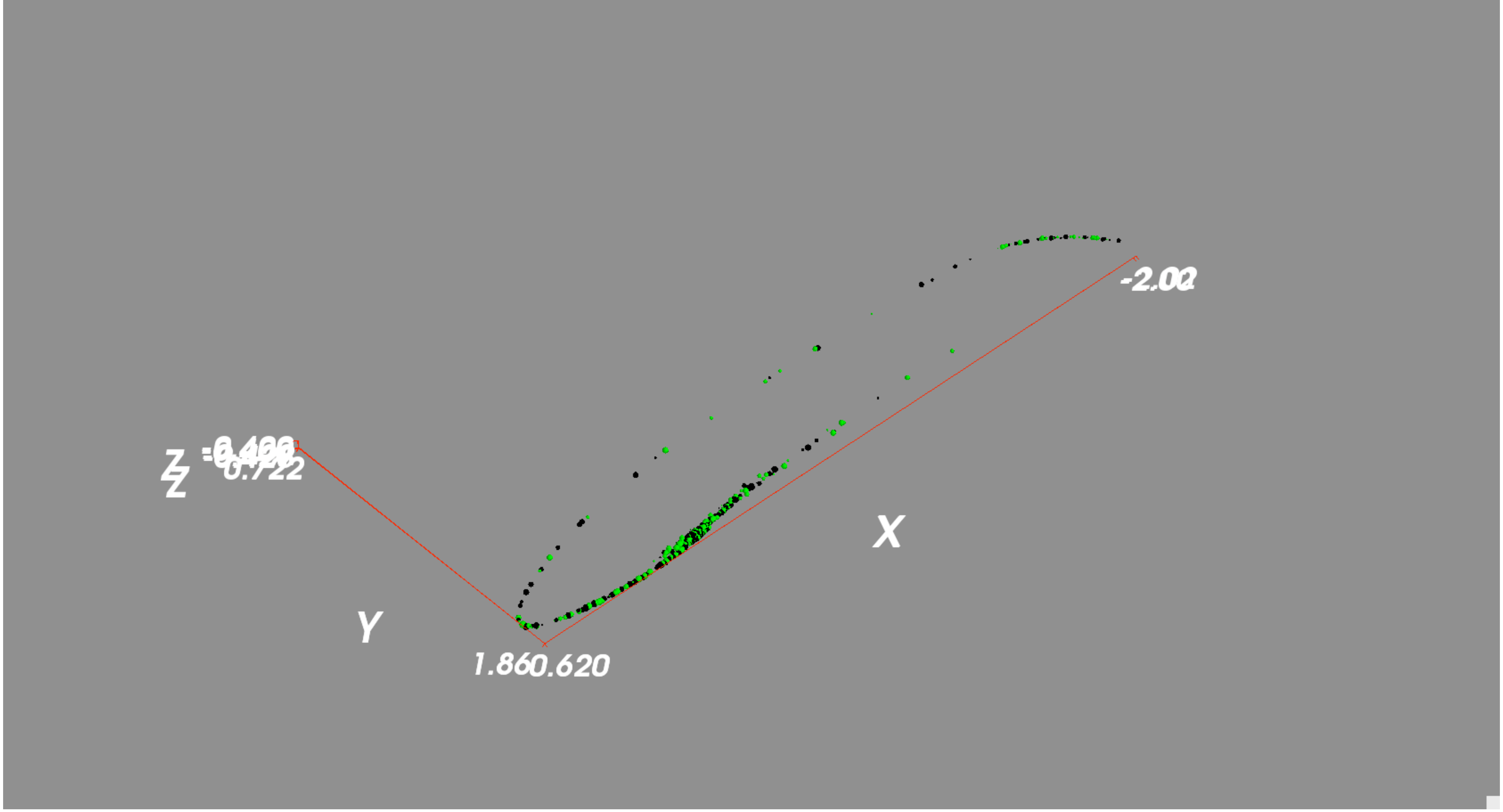


320 steps $k_f = 0.00216$

Green: IC = (0.446751, 5.275282, 0.393890)

Black: IC = (0.446780, 5.275270, 0.393895)

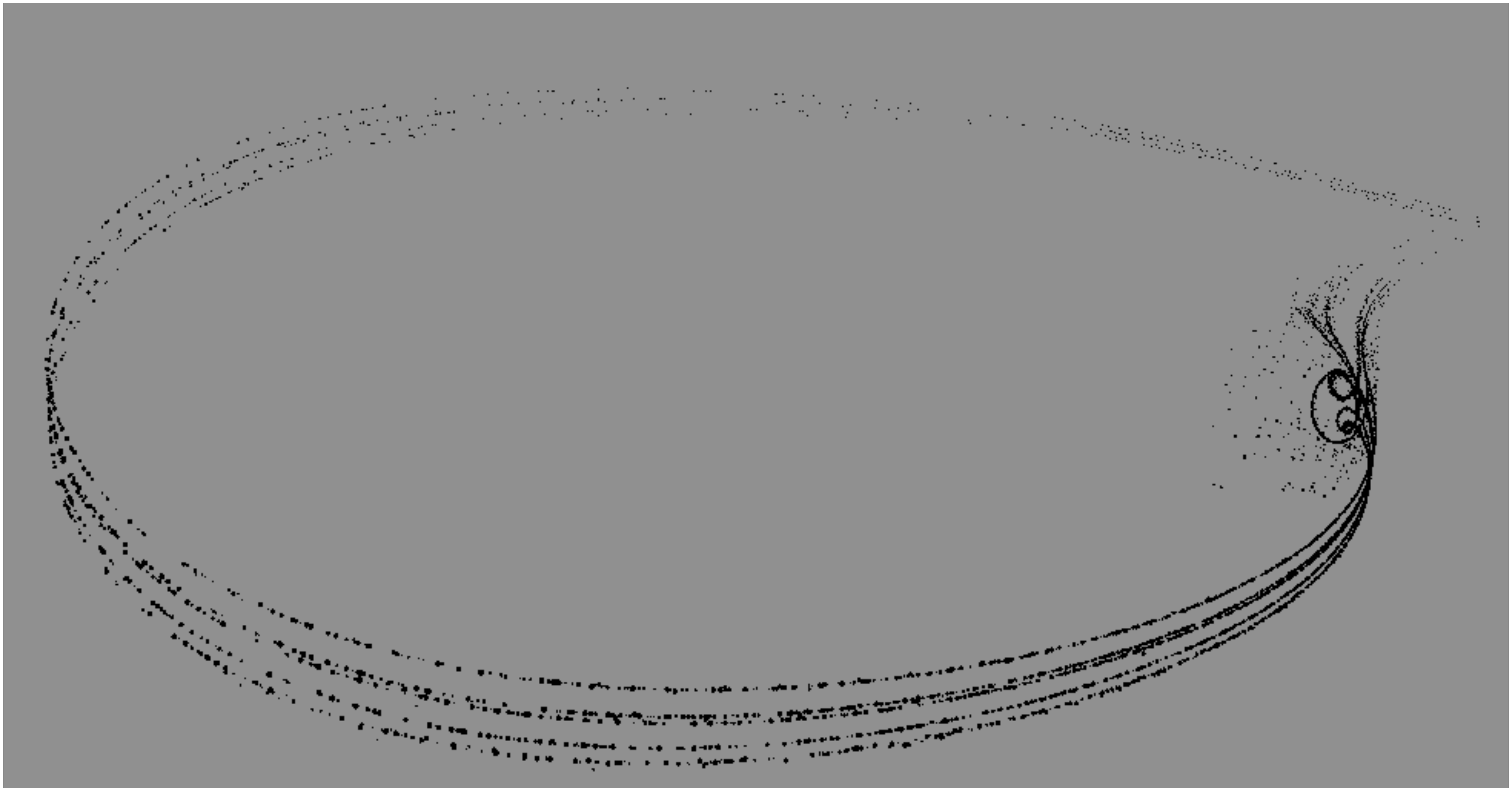
sensitive dependence on initial conditions



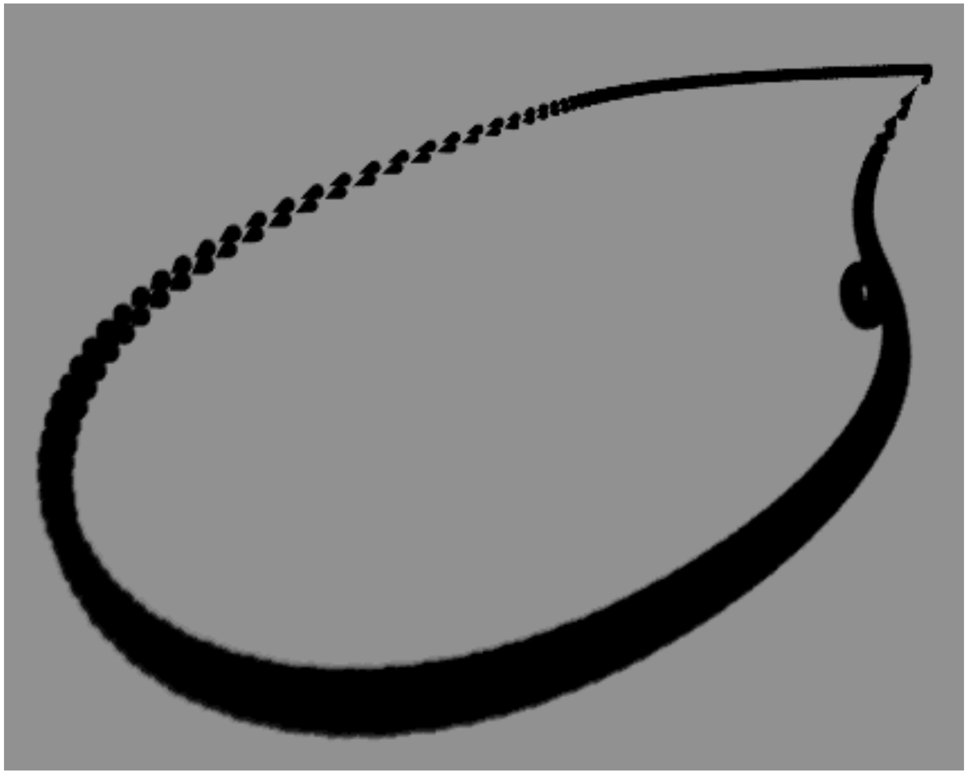
640 steps $k_f = 0.00216$

Green: IC = (0.446751, 5.275282, 0.393890)

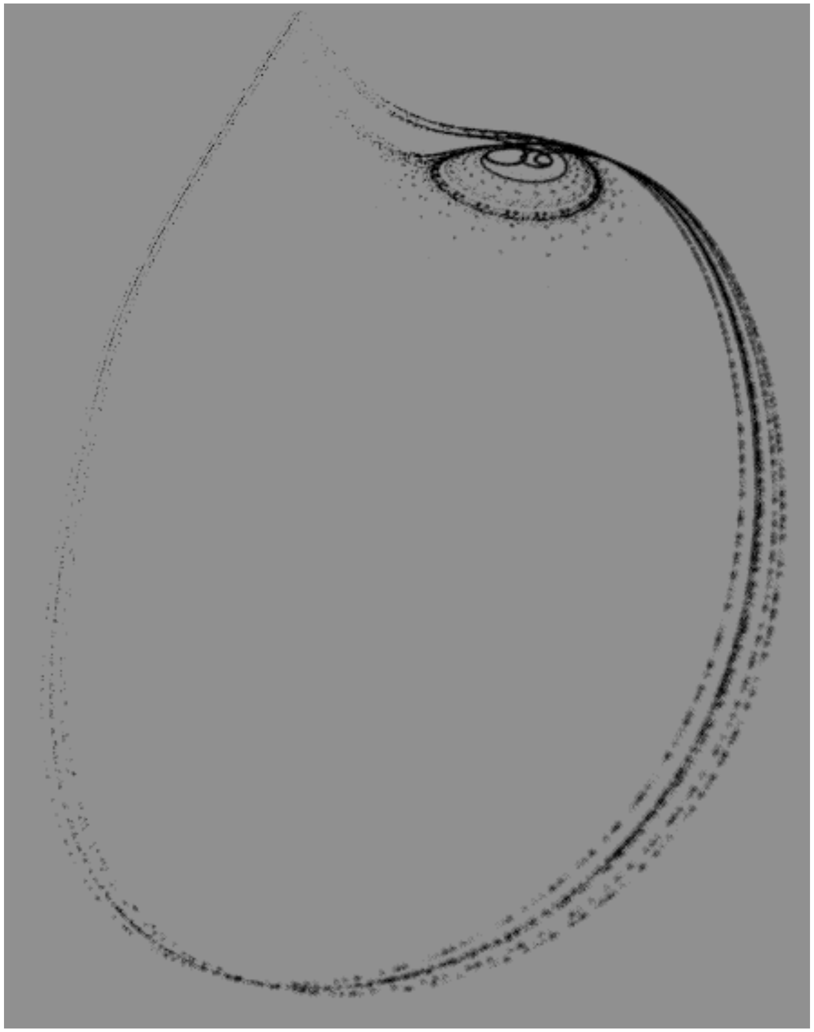
Black: IC = (0.446780, 5.275270, 0.393895)



$k_f = 0.0020798$

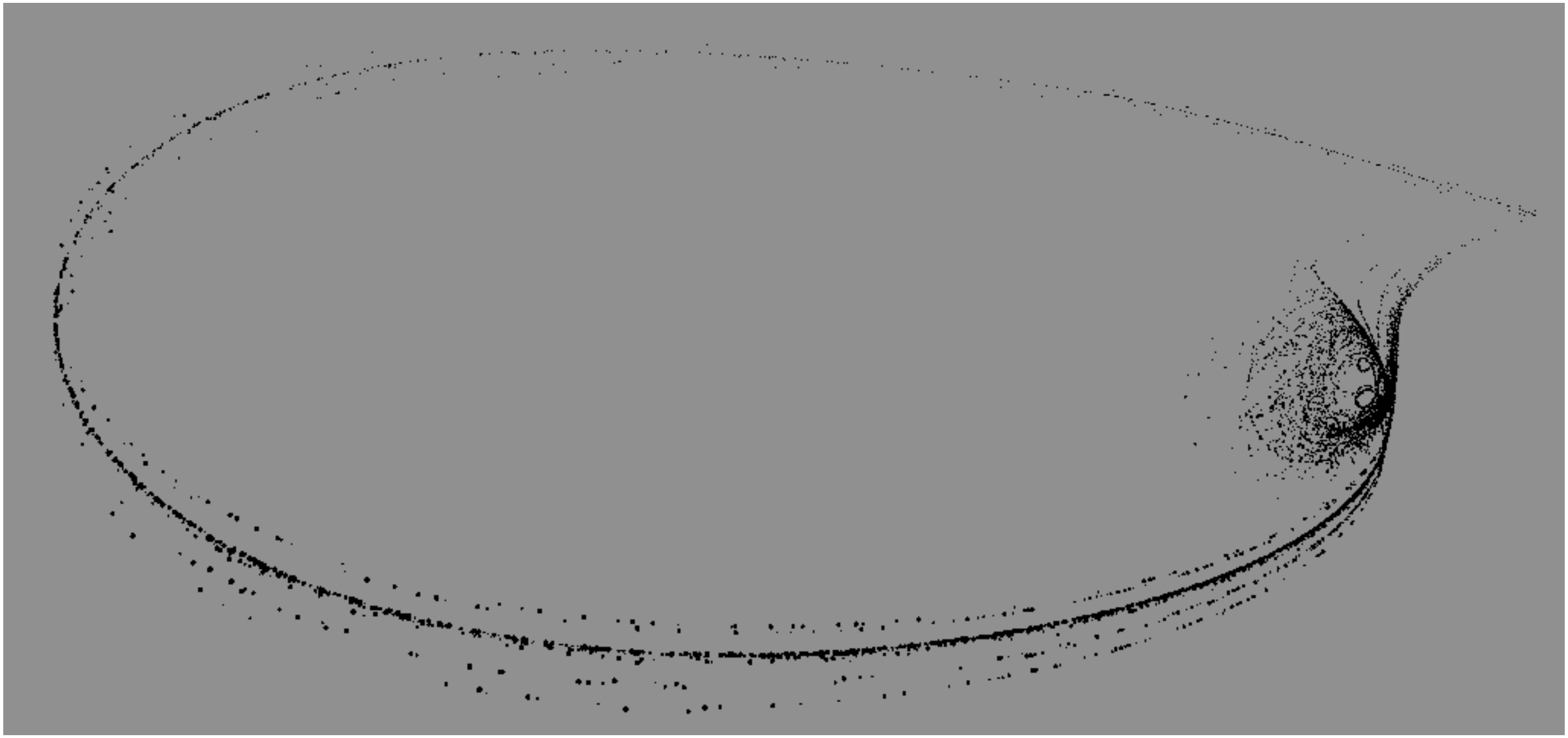


~ 1000 iterations

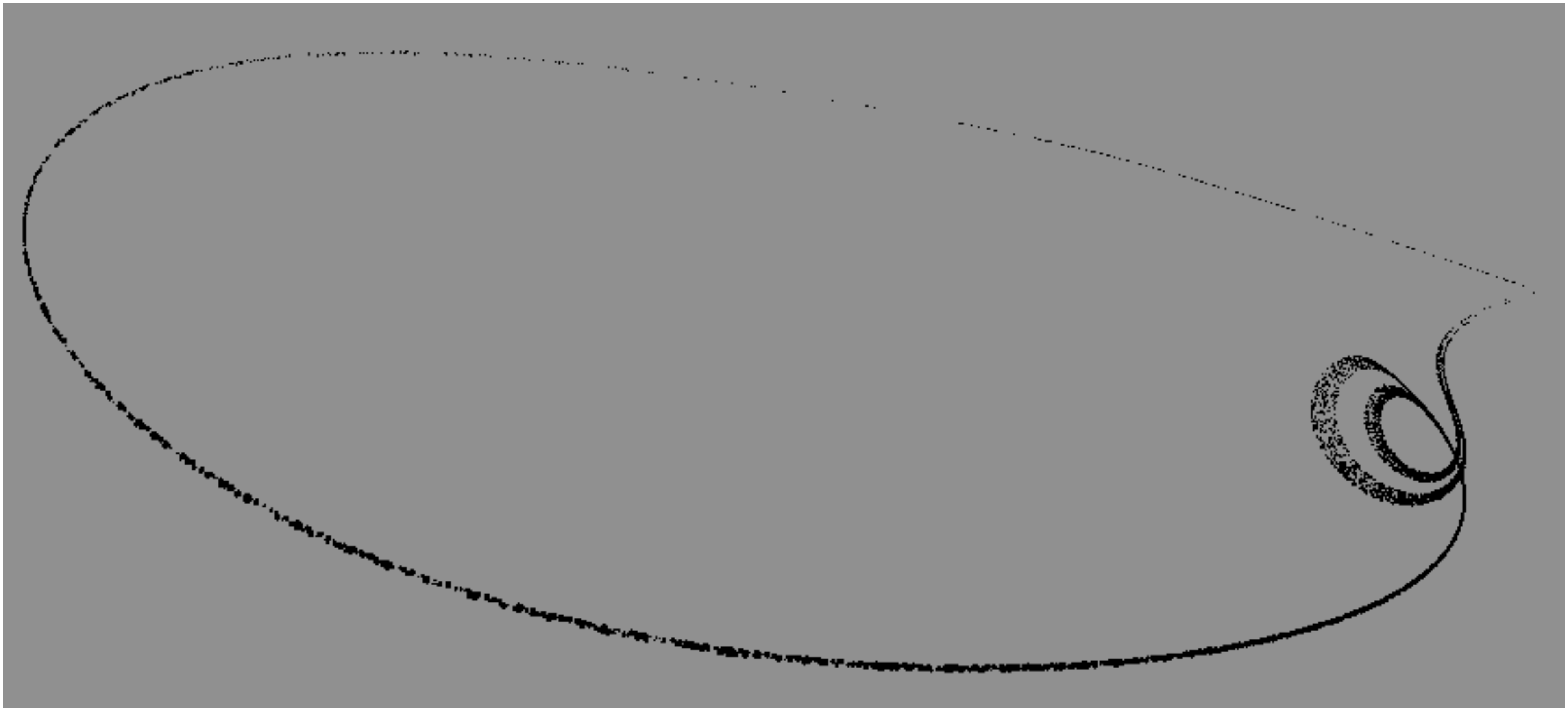


~ 20000 iterations

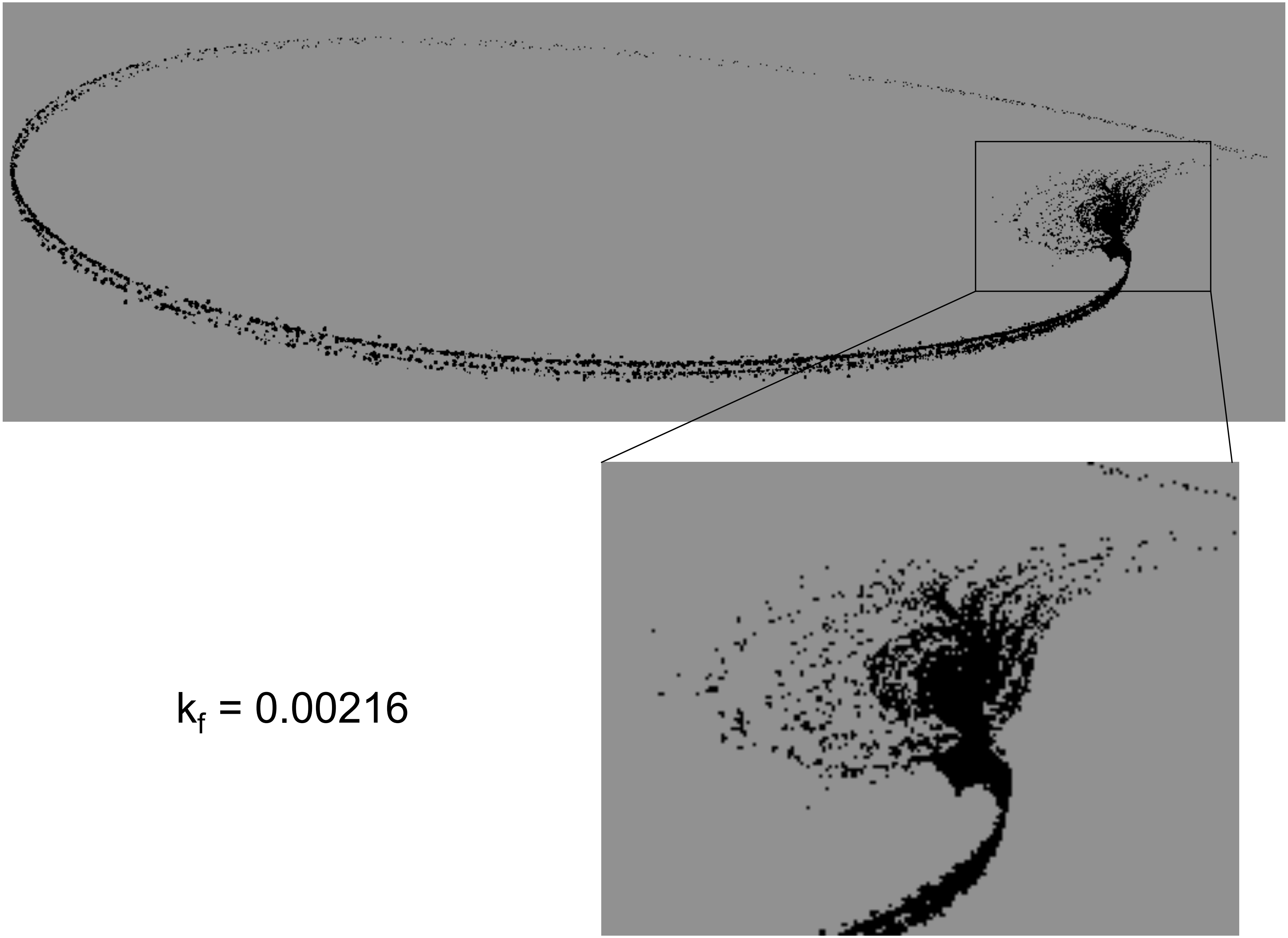
$k_f = 0.00208$



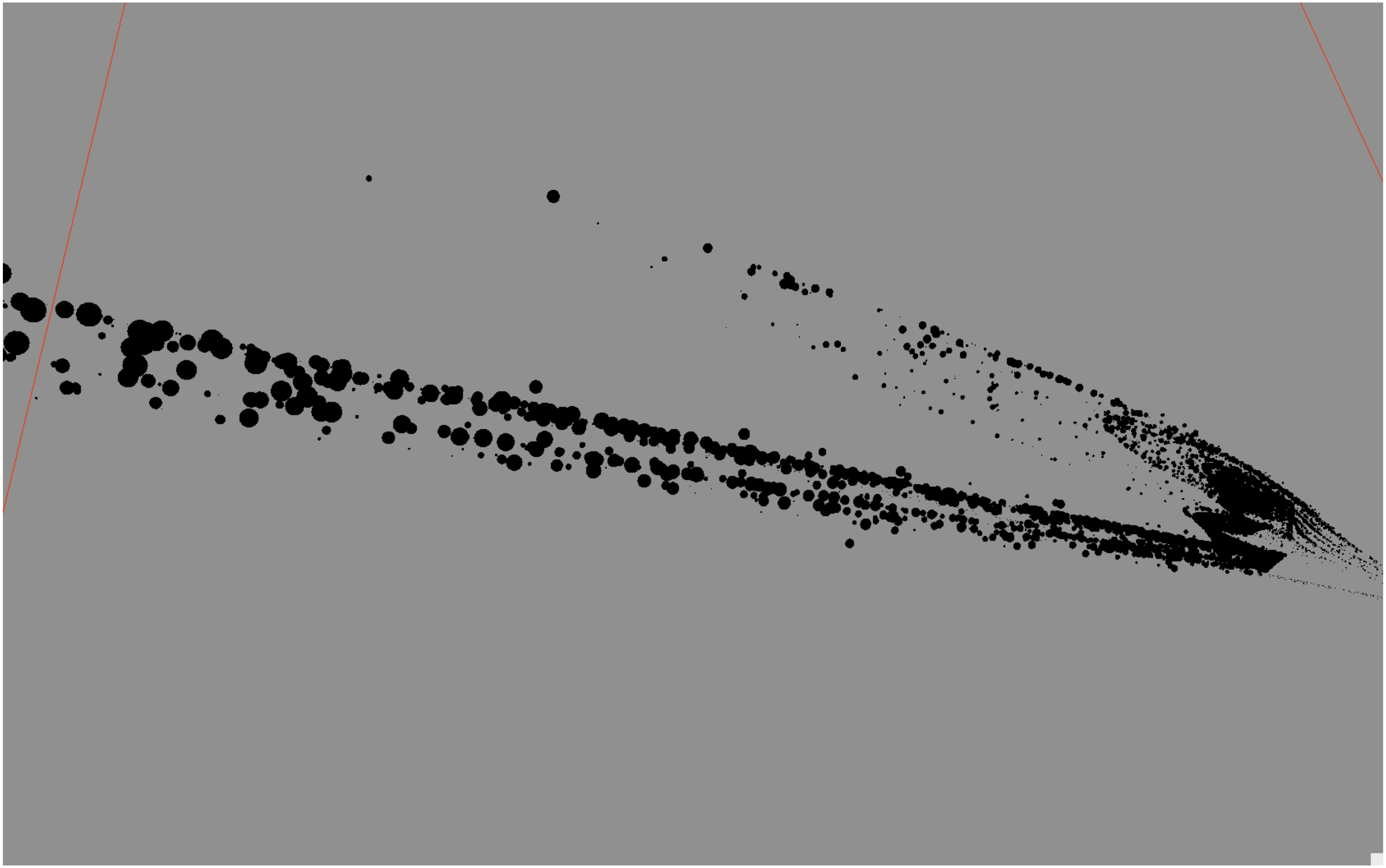
$k_f = 0.002081$



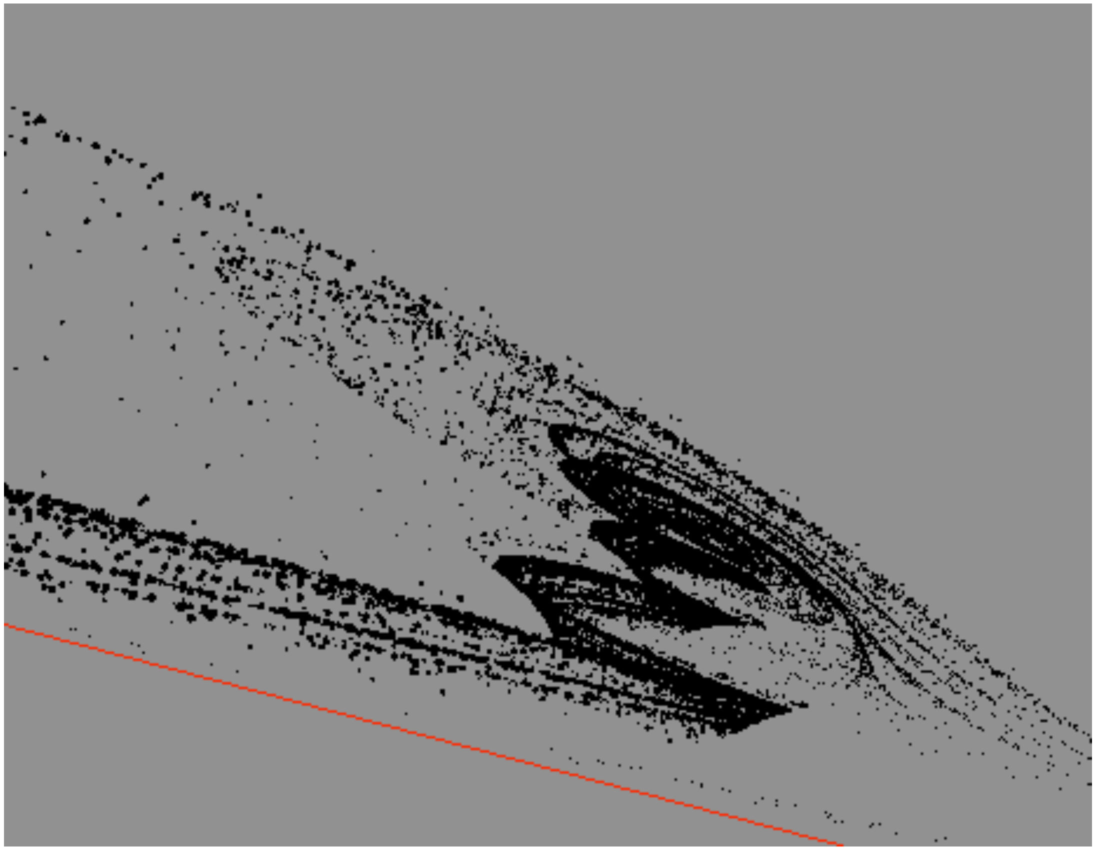
$k_f = 0.00208105$



$k_f = 0.00216$



$k_f = 0.00216$



$k_f = 0.00216$

Caution: Stiff ODEs

- Runge-Kutta fails (At least without a variable step-size)
- Popular method for integrating these ODE’s is known as the GEAR method
- In Python, one can use SciPy’s integrate.odeint()
- Orbit Diagrams in MayaVi can take a very long time

Thanks

Questions?