

分岐現象と非線形振動子

分岐理論とは

力学系においてパラメータを連続的に変化させていったときに、解の存在・非存在、安定・不安定など定性的な性質が変わる点に着目し、その特徴を議論する方法

おもな分岐の種類

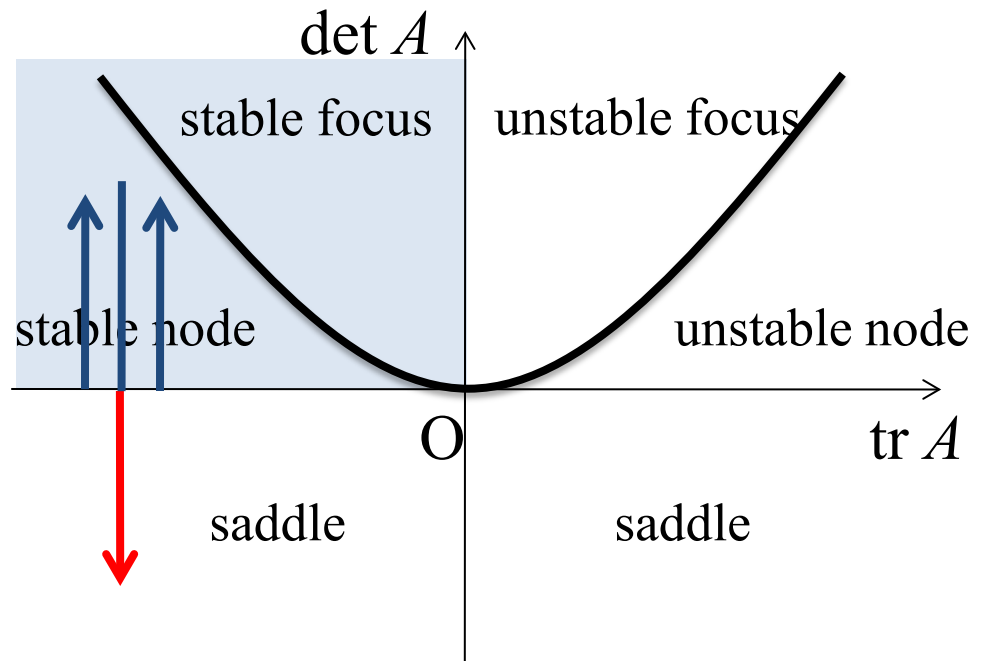
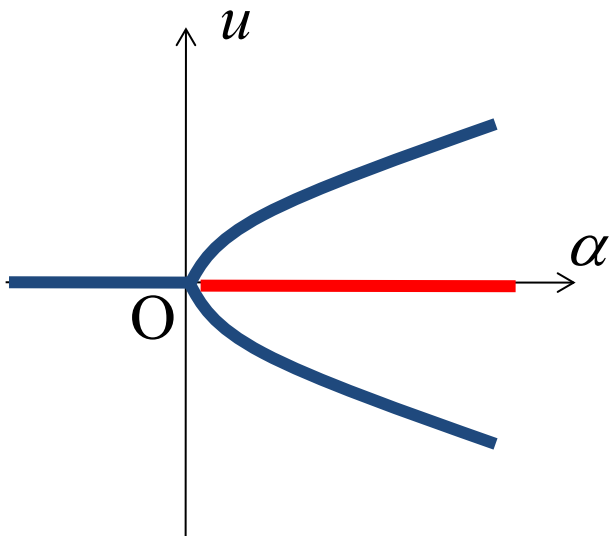
- ピッチフォーク分岐
- サドル・ノード分岐
- トランスクリティカル分岐 (安定性交替分岐)
- ホップ分岐

- ピッチフォーク分岐

$$\frac{dx}{dt} = ax - x^3$$

固定点 : $x = 0, \pm\sqrt{a}$ ($a > 0$)

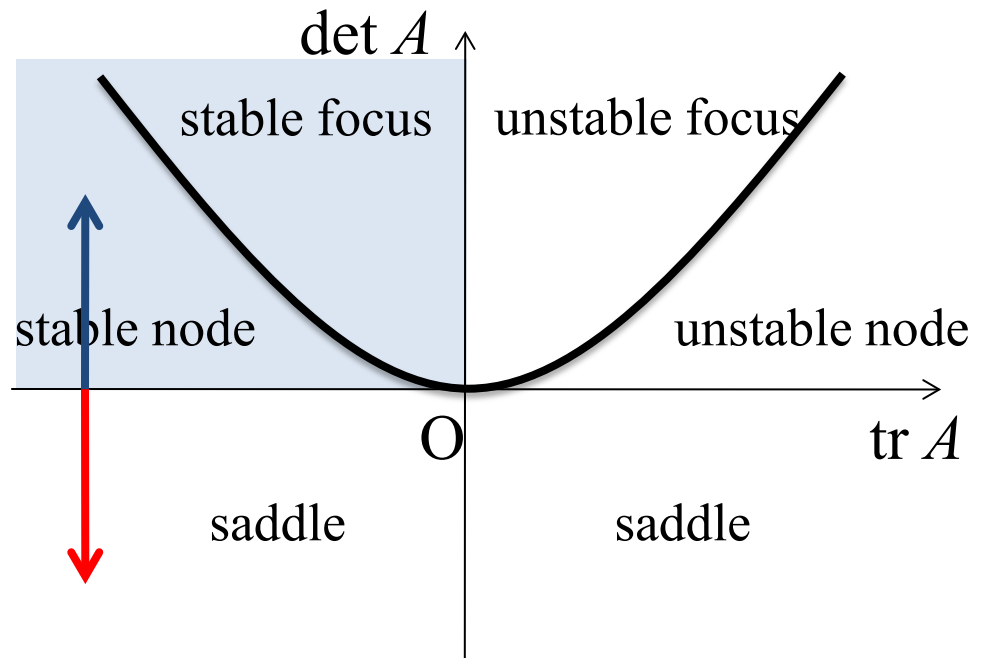
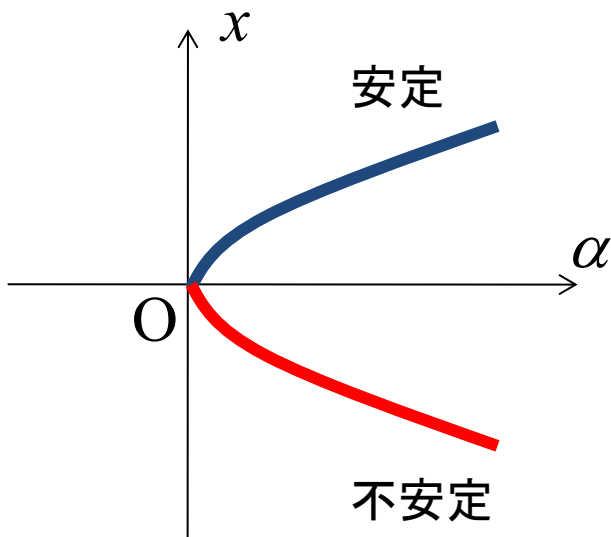
$x = 0$ ($a \leq 0$)



- サドル・ノード分岐

$$\frac{dx}{dt} = a - x^2$$

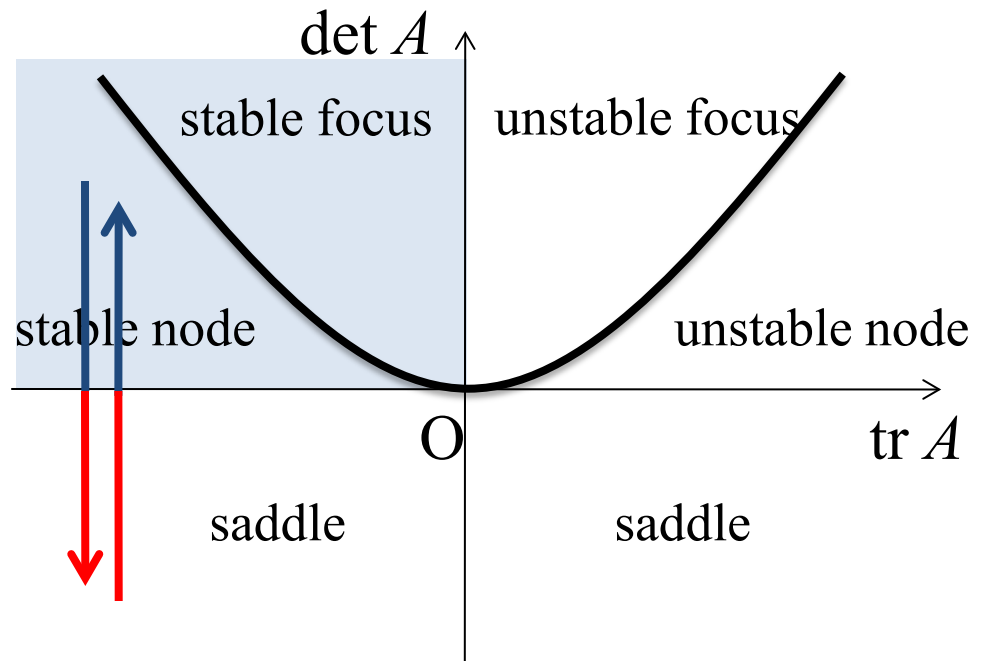
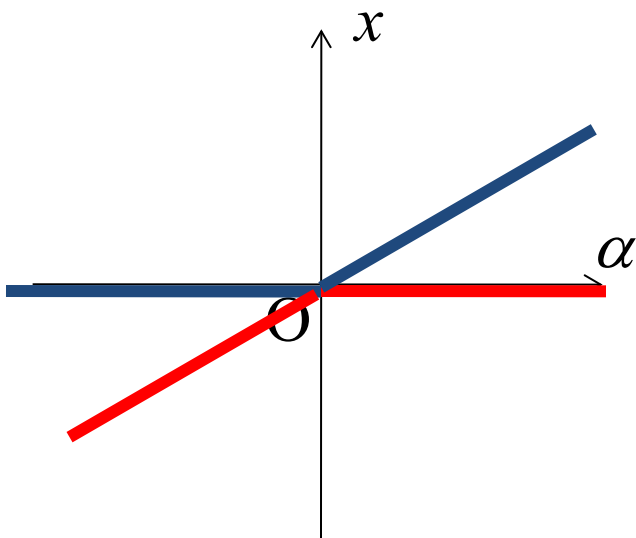
固定点 : $x = \pm\sqrt{a}$ ($a \geq 0$)



- トランスクリティカル分岐 (安定性交替分岐)

$$\frac{dx}{dt} = ax - x^2$$

固定点: $x = 0, a$

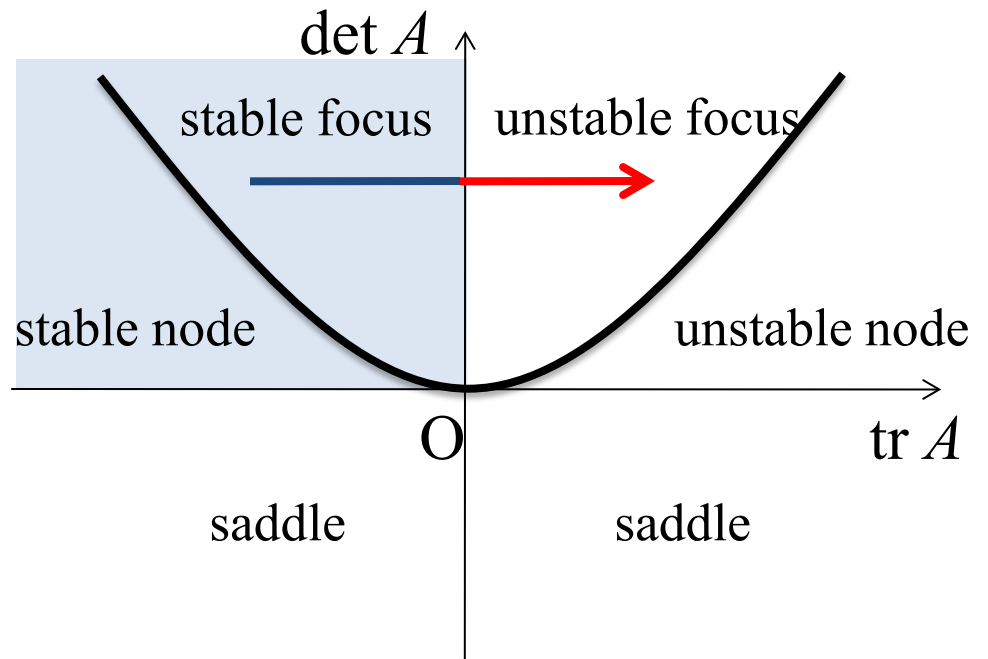
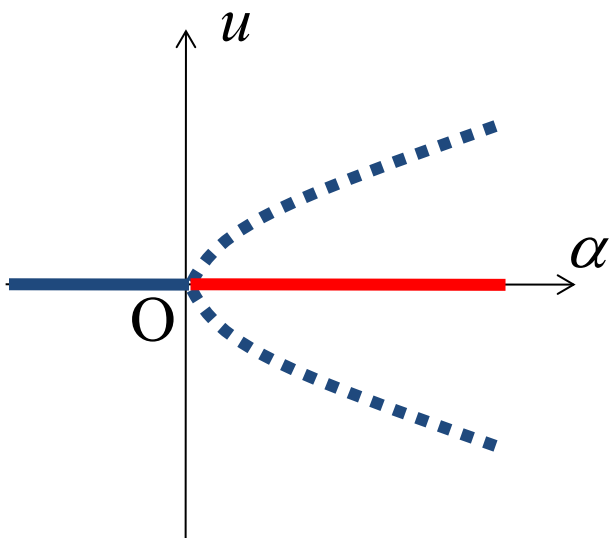


- ホップ分岐

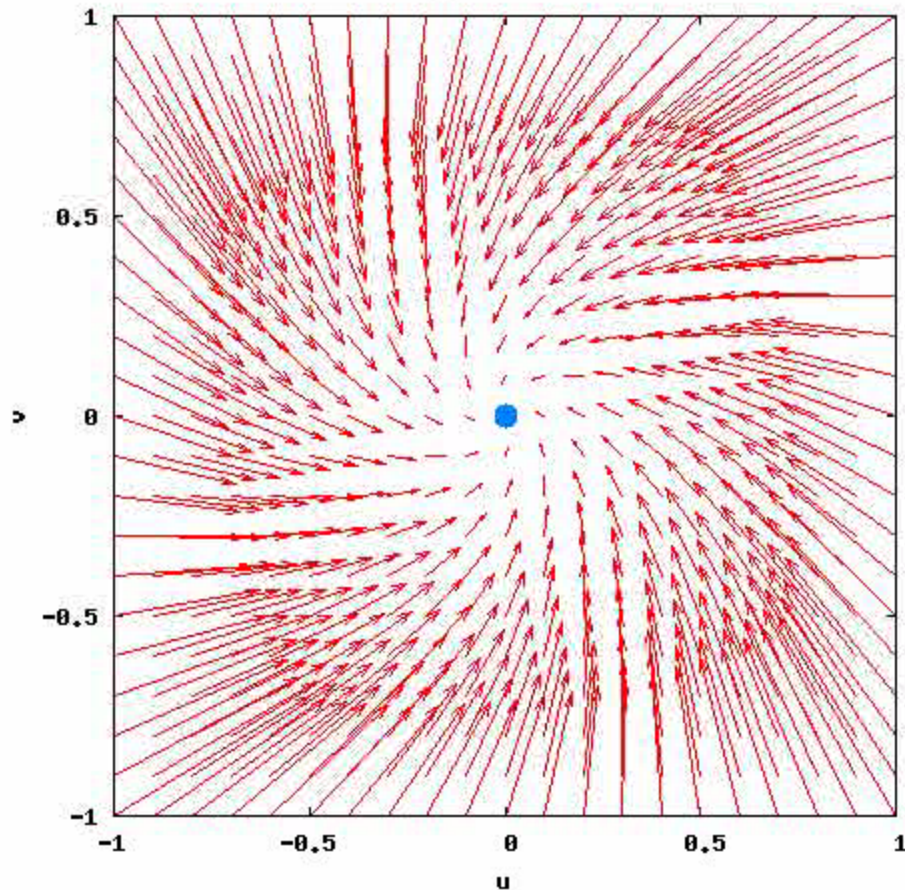
$$\frac{dx}{dt} = ax - \omega y - (x^2 + y^2)(x - by)$$

$$\frac{dy}{dt} = ay + \omega x - (x^2 + y^2)(y + bx)$$

固定点 : $x = y = 0$



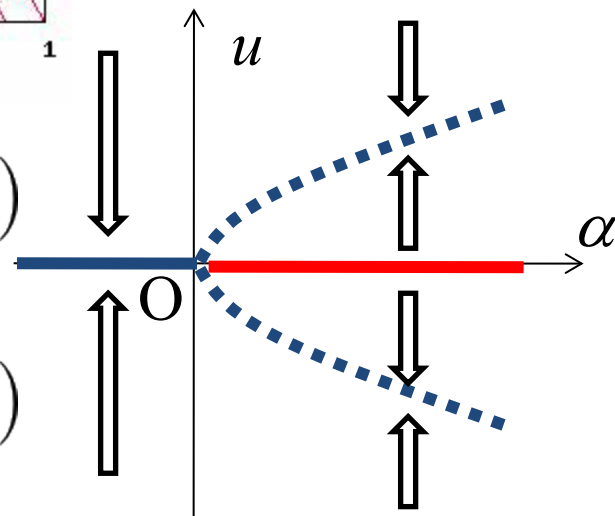
alpha = -2.00



$b = 0$

$$\frac{dx}{dt} = ax - \omega y - (x^2 + y^2)(x - by)$$

$$\frac{dy}{dt} = ay + \omega x - (x^2 + y^2)(y + bx)$$

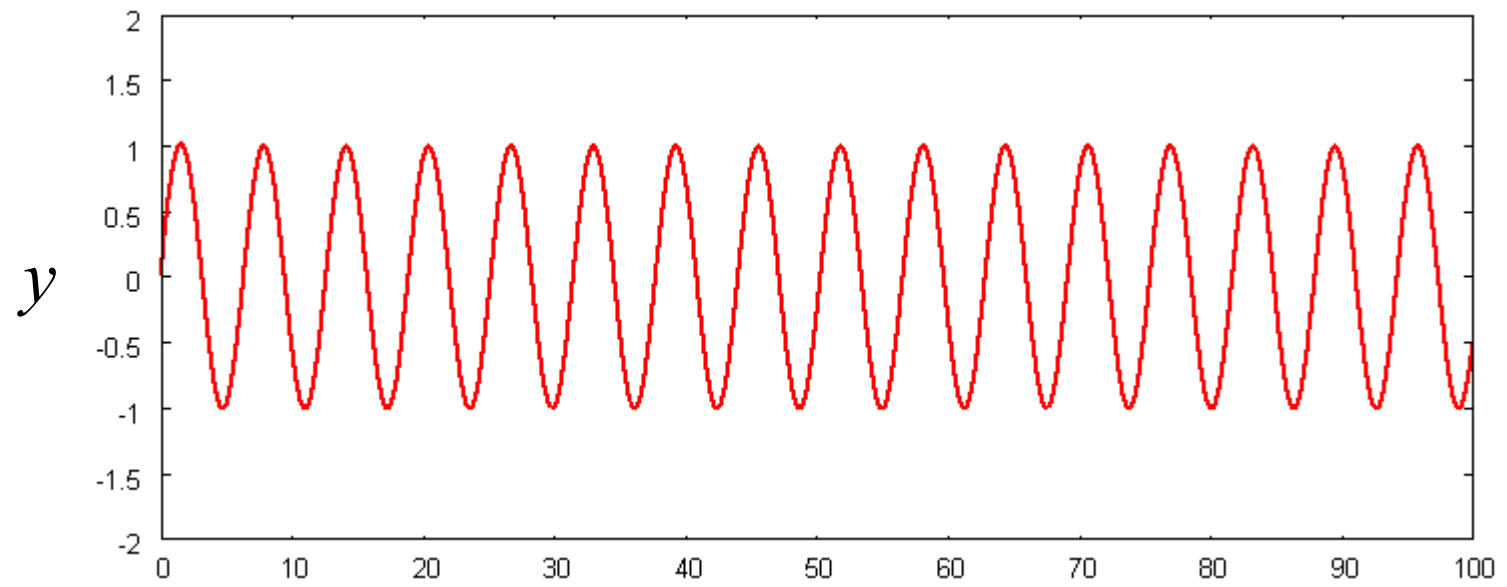
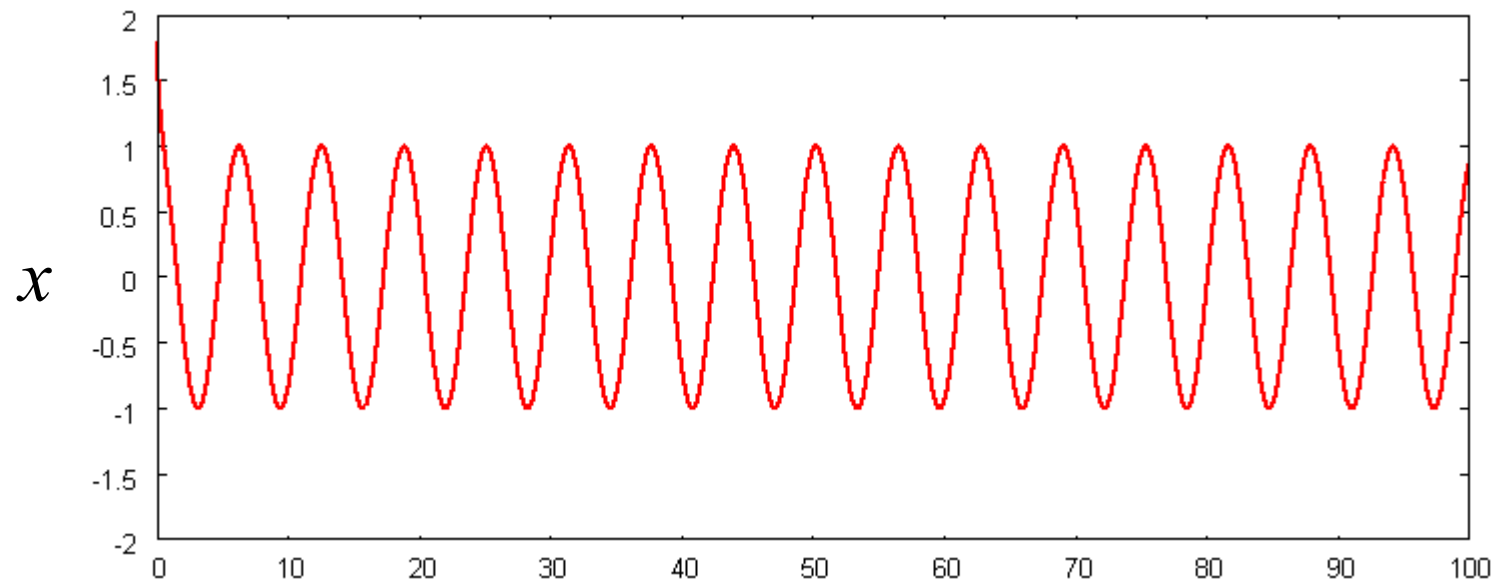


Stuart- Landau方程式の数値計算(プログラム)

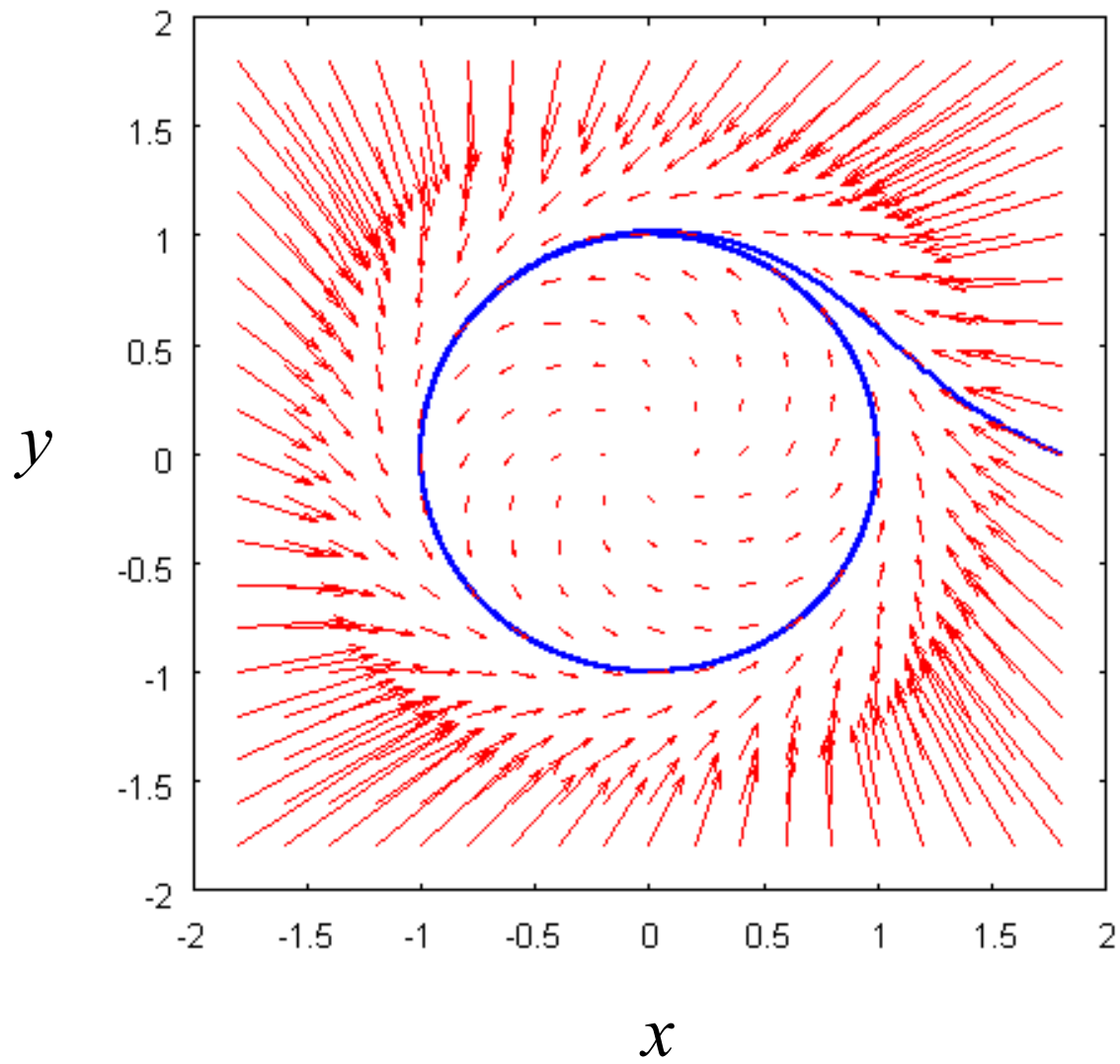
$$\frac{dx}{dt} = ax - \omega y - (x^2 + y^2)(x - by)$$

$$\frac{dy}{dt} = ay + \omega x - (x^2 + y^2)(y + bx)$$

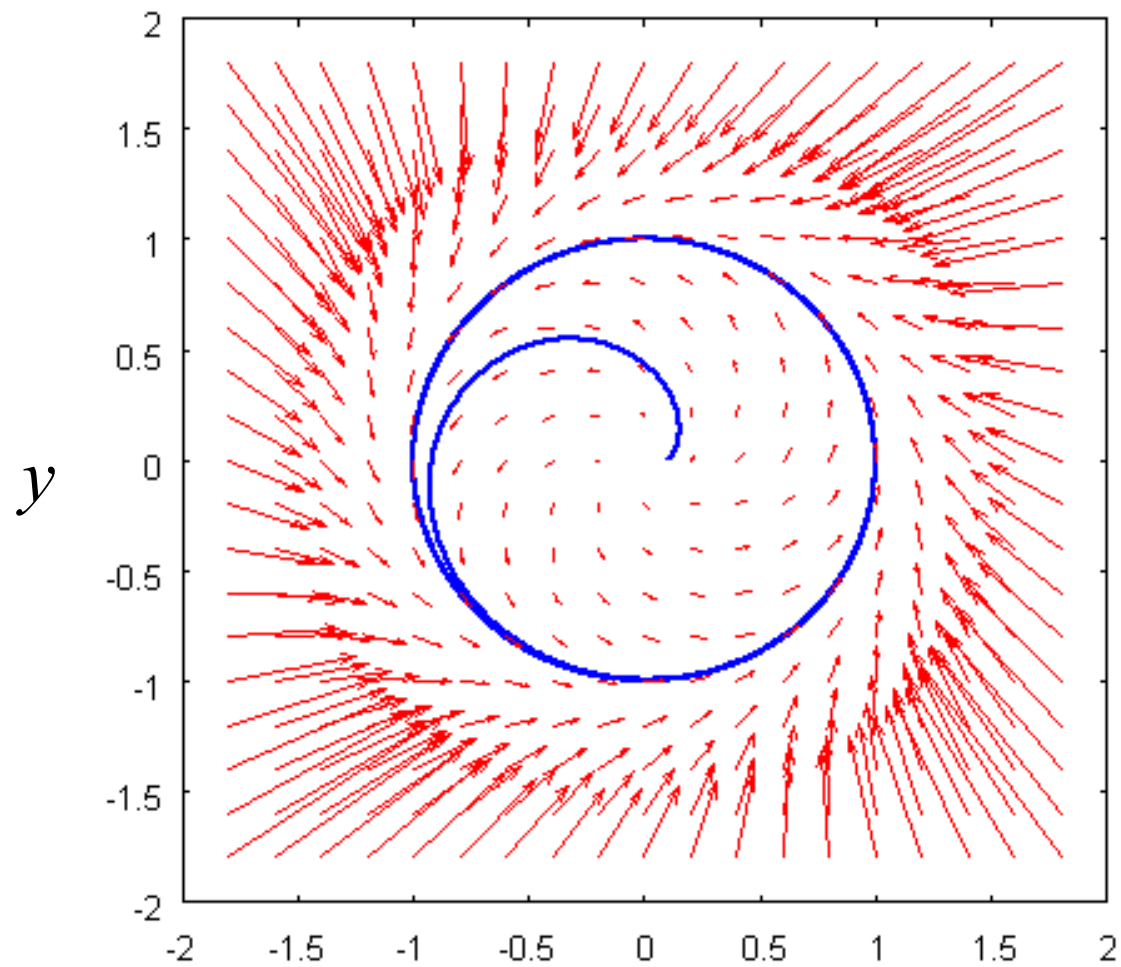




time



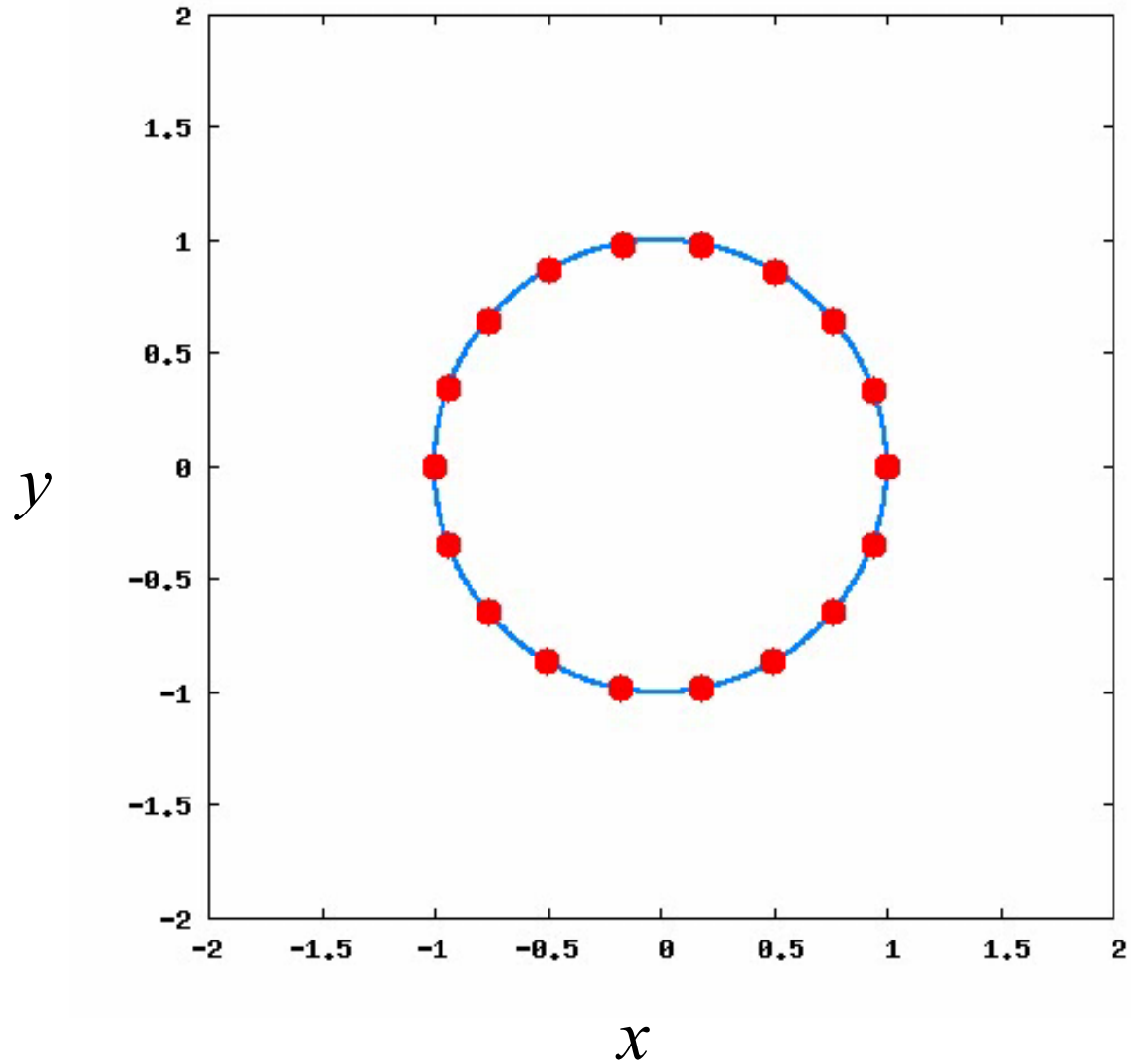
初期値を変えても

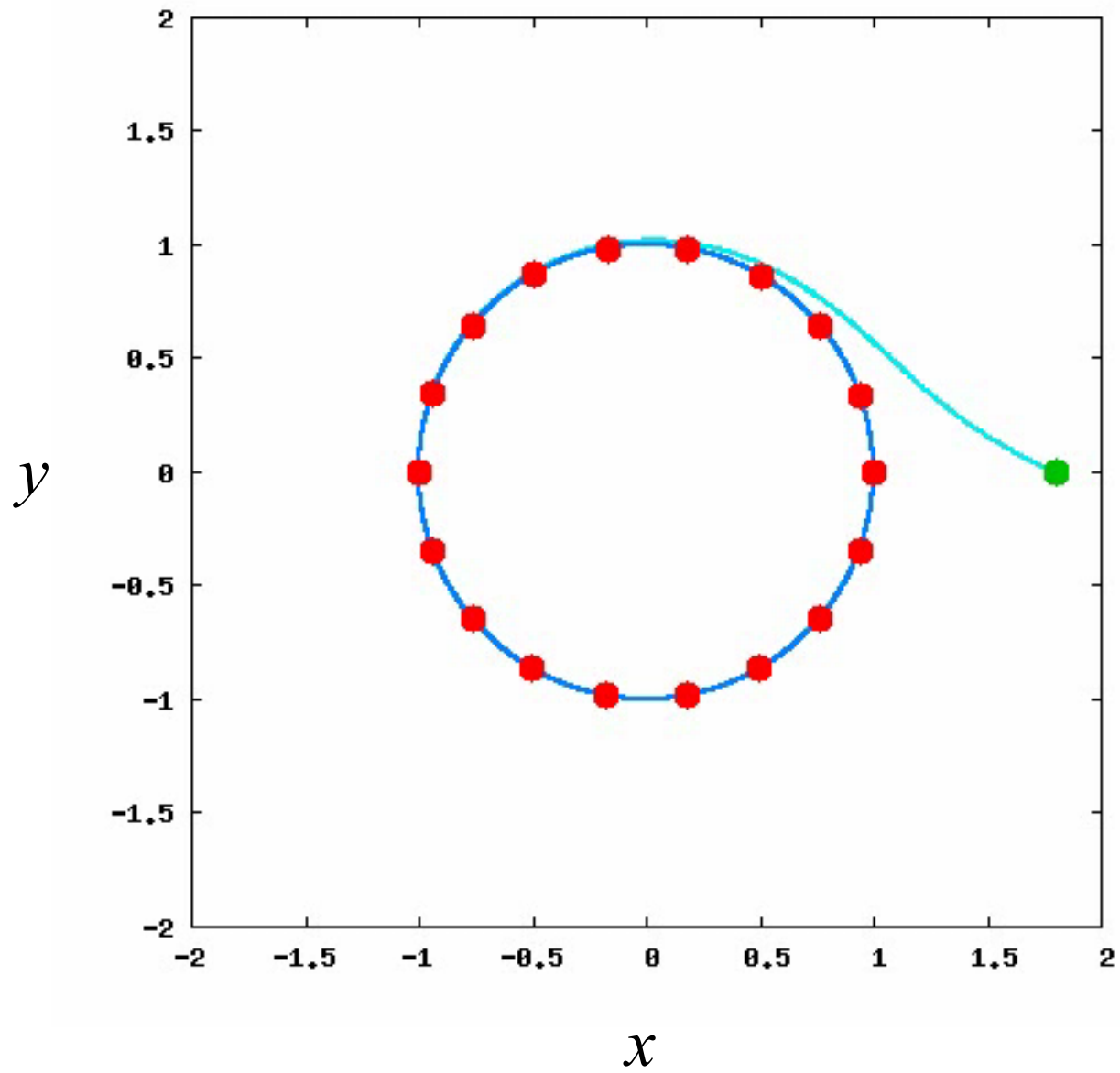


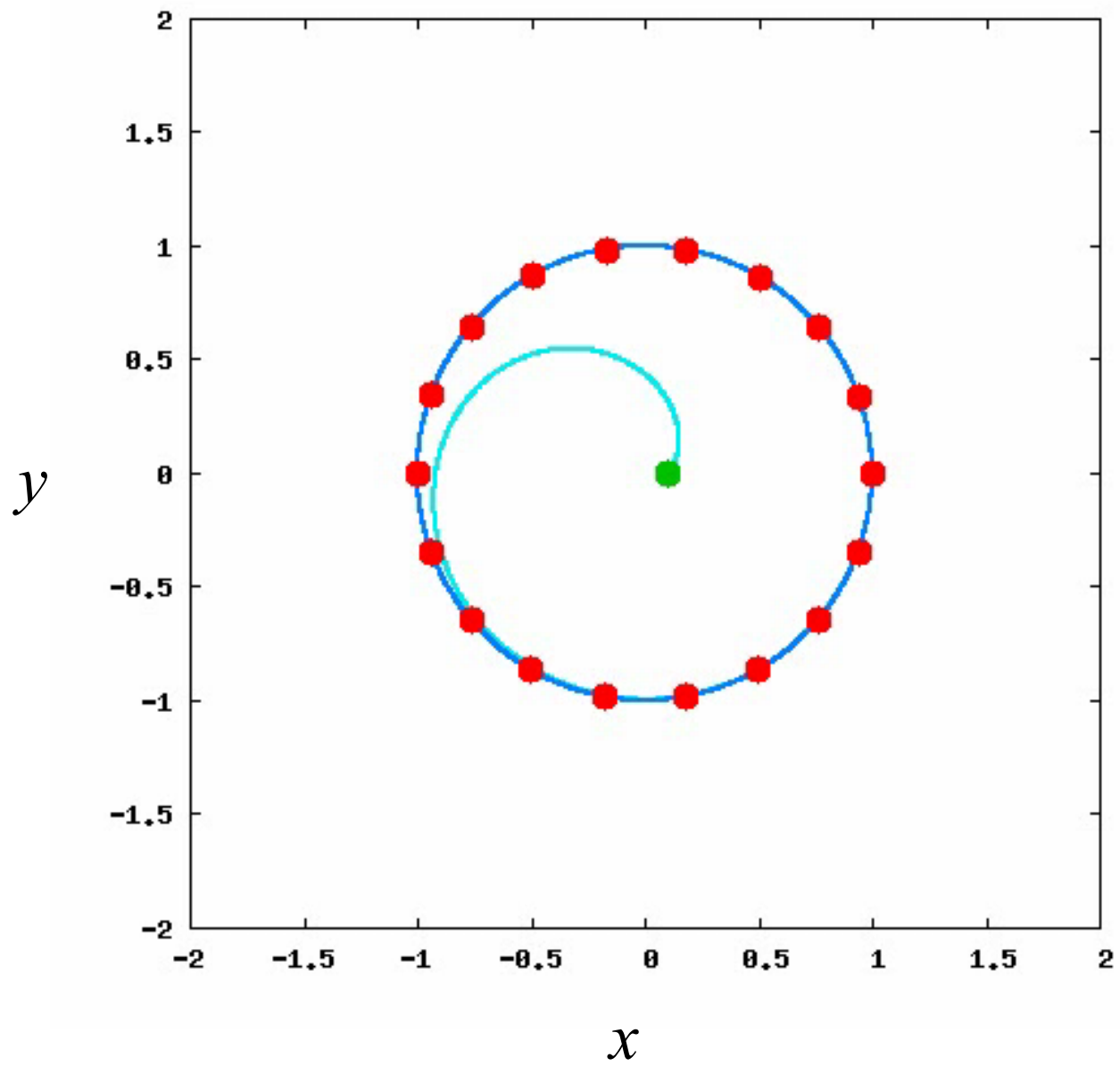
x

Limit Cycle (極限軌道)

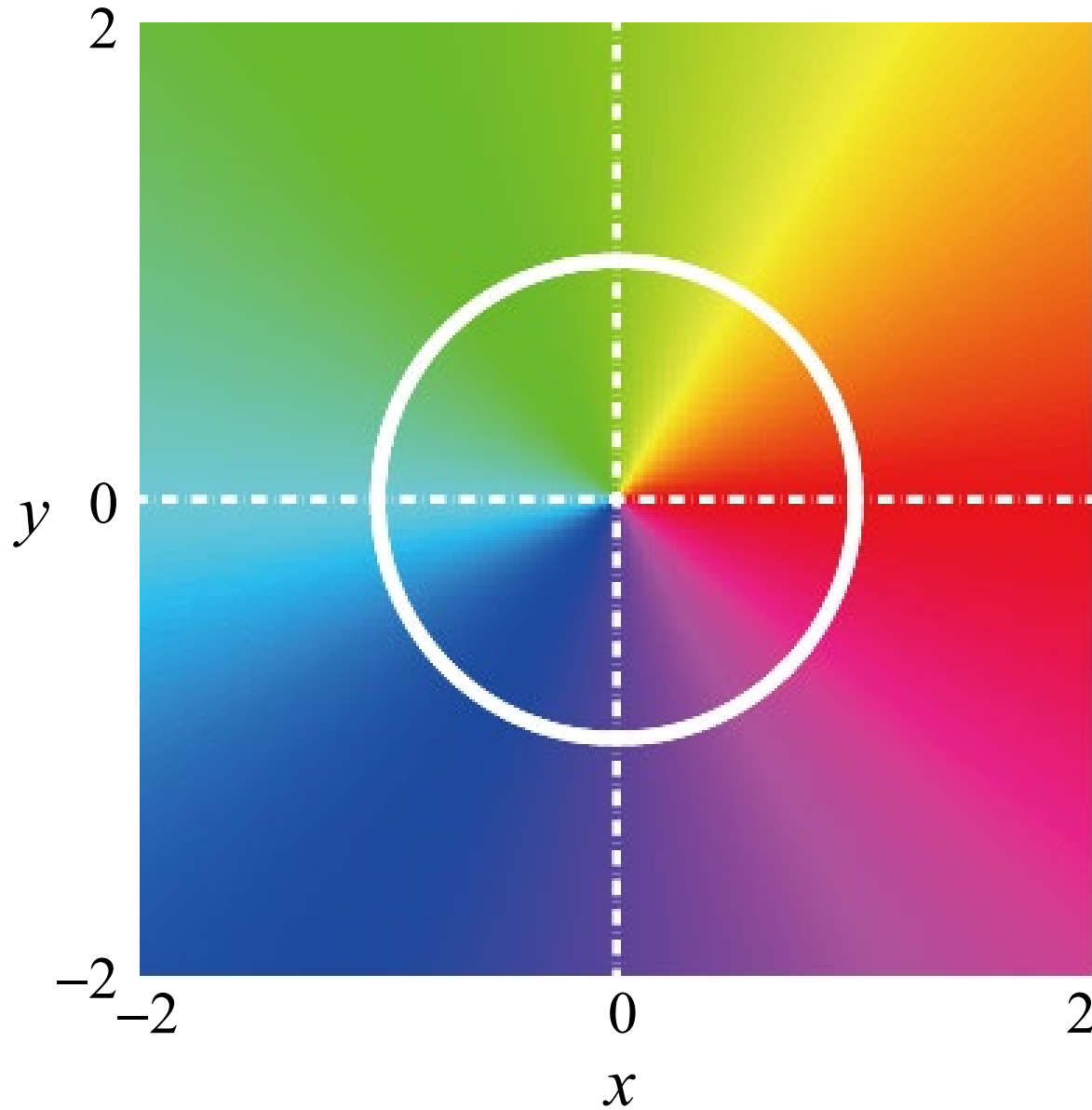
リミットサイクル上の運動







等位相面



$$\theta = \arctan\left(\frac{y}{x}\right)$$

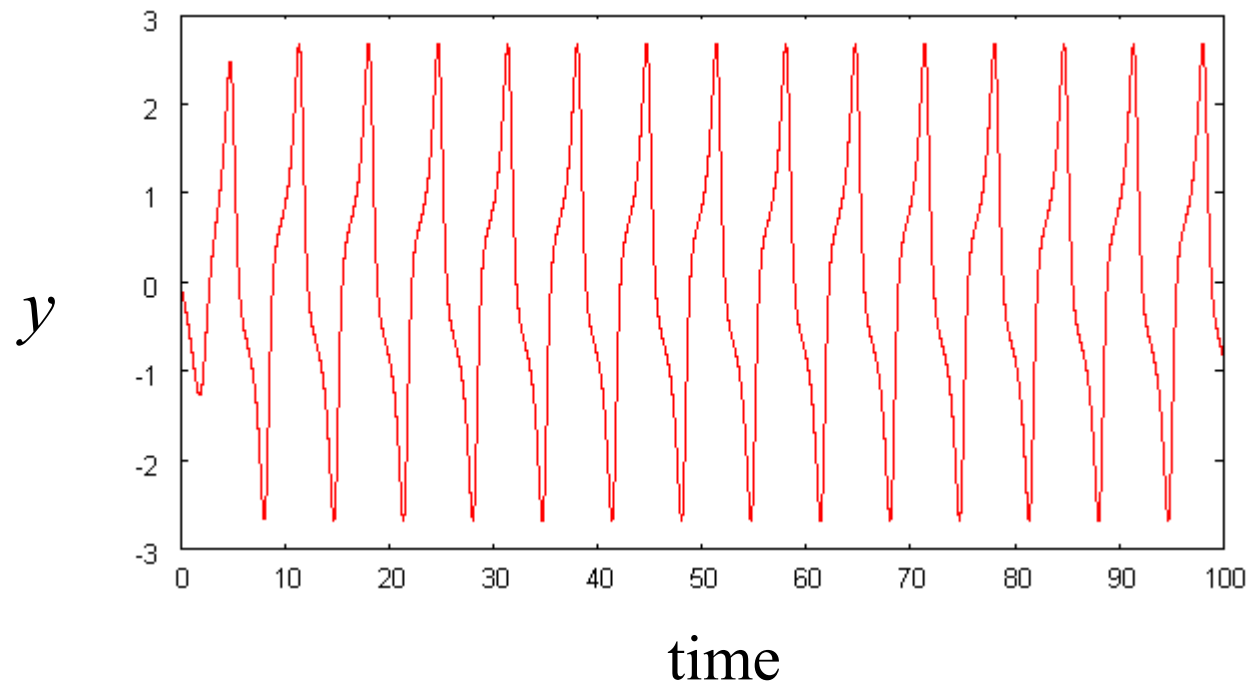
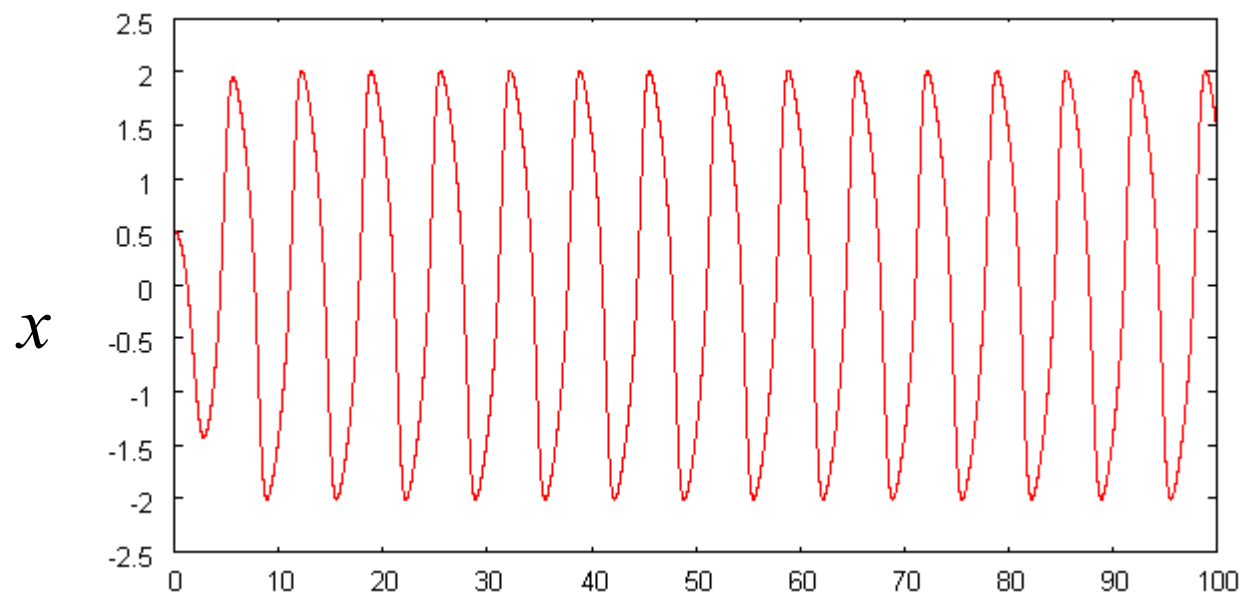
van del Pol 方程式 ~ 丸くなくても...

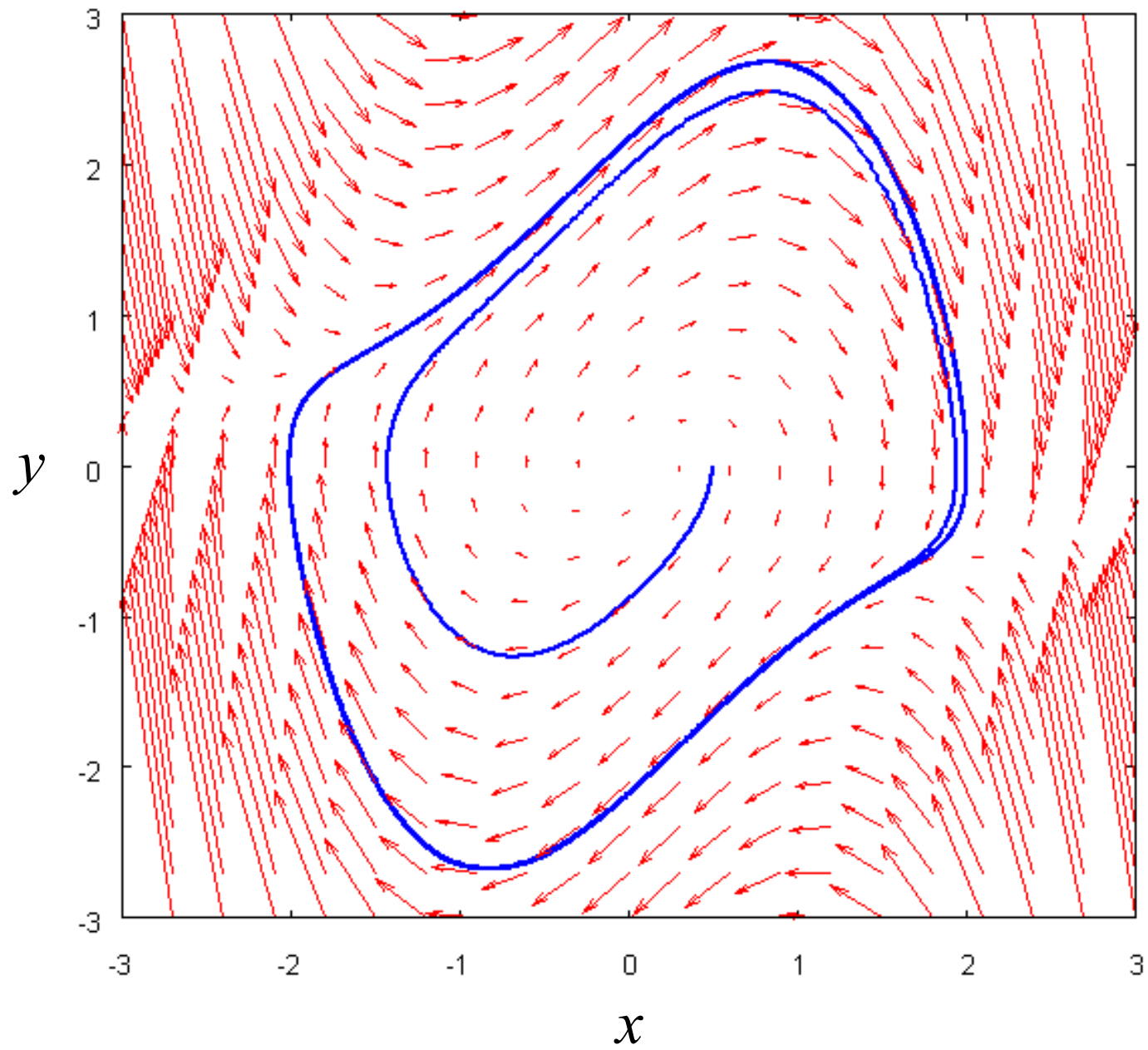
$$\frac{d^2 x}{dt^2} + \alpha(x^2 - 1)\frac{dx}{dt} + x = 0$$

$$\left\{ \begin{array}{l} \frac{dx}{dt} = y \\ \frac{dy}{dt} = -\alpha(x^2 - 1)y - x \end{array} \right.$$

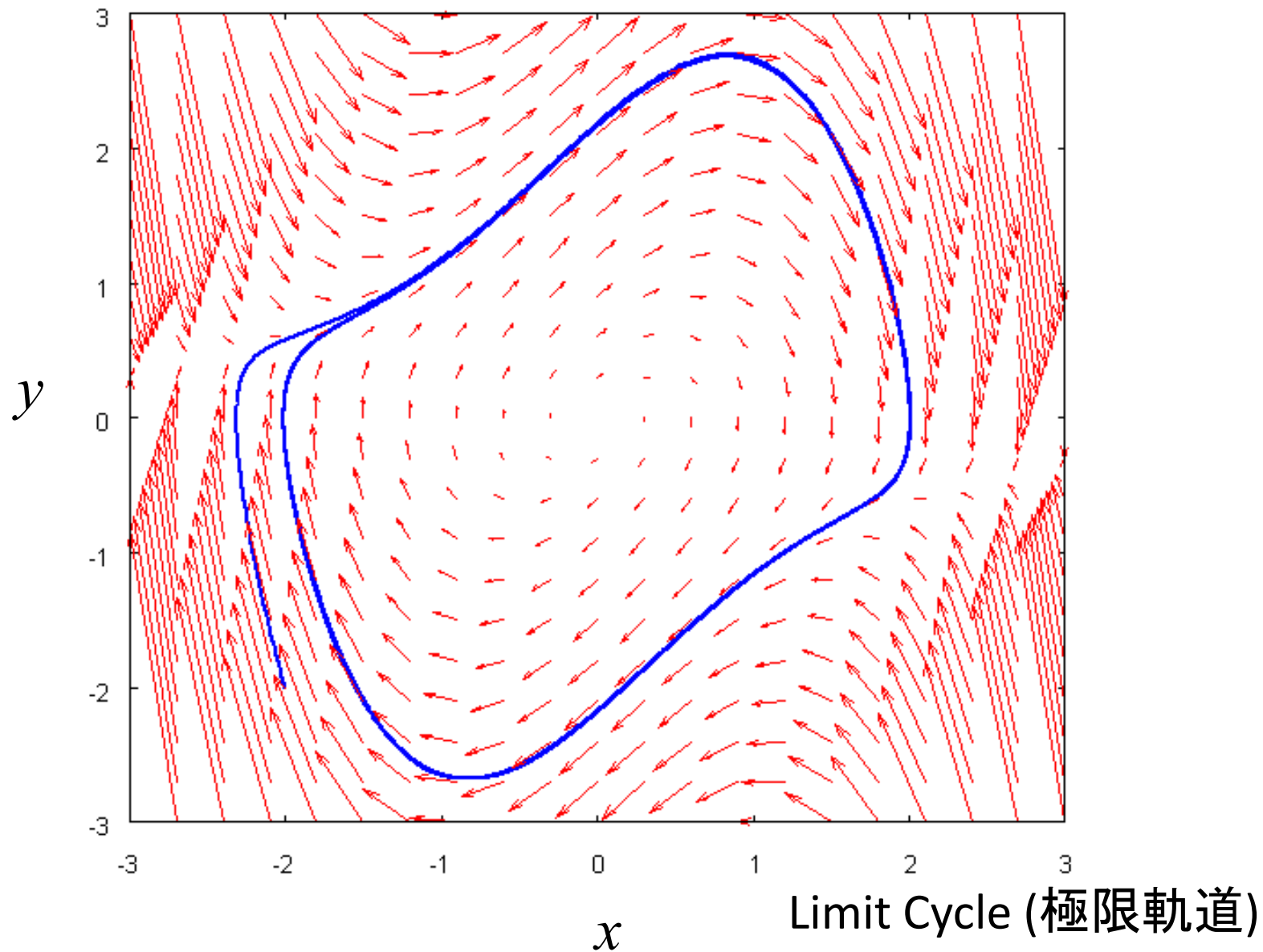
van der Pol 方程式の数値計算(プログラム)



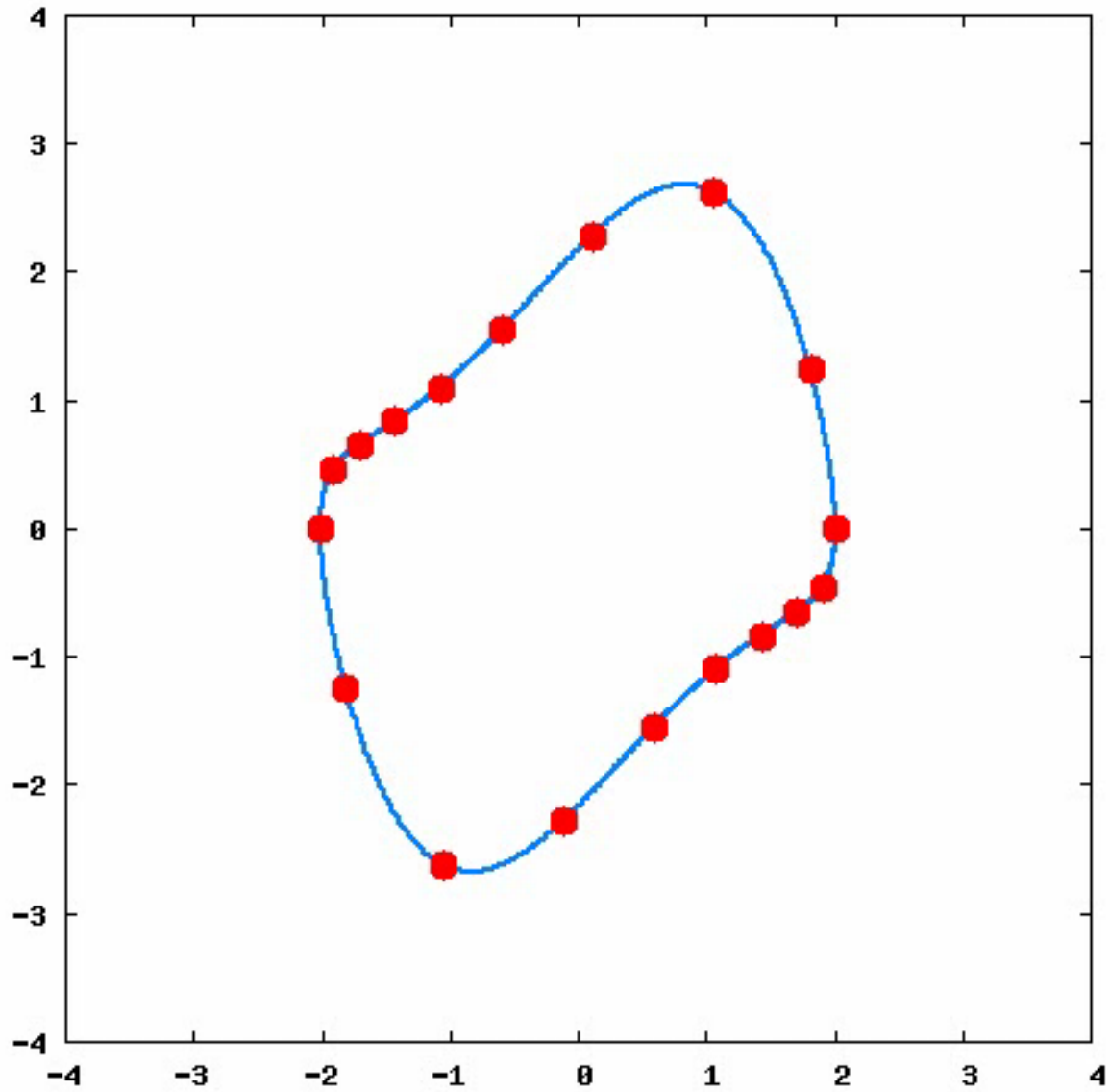




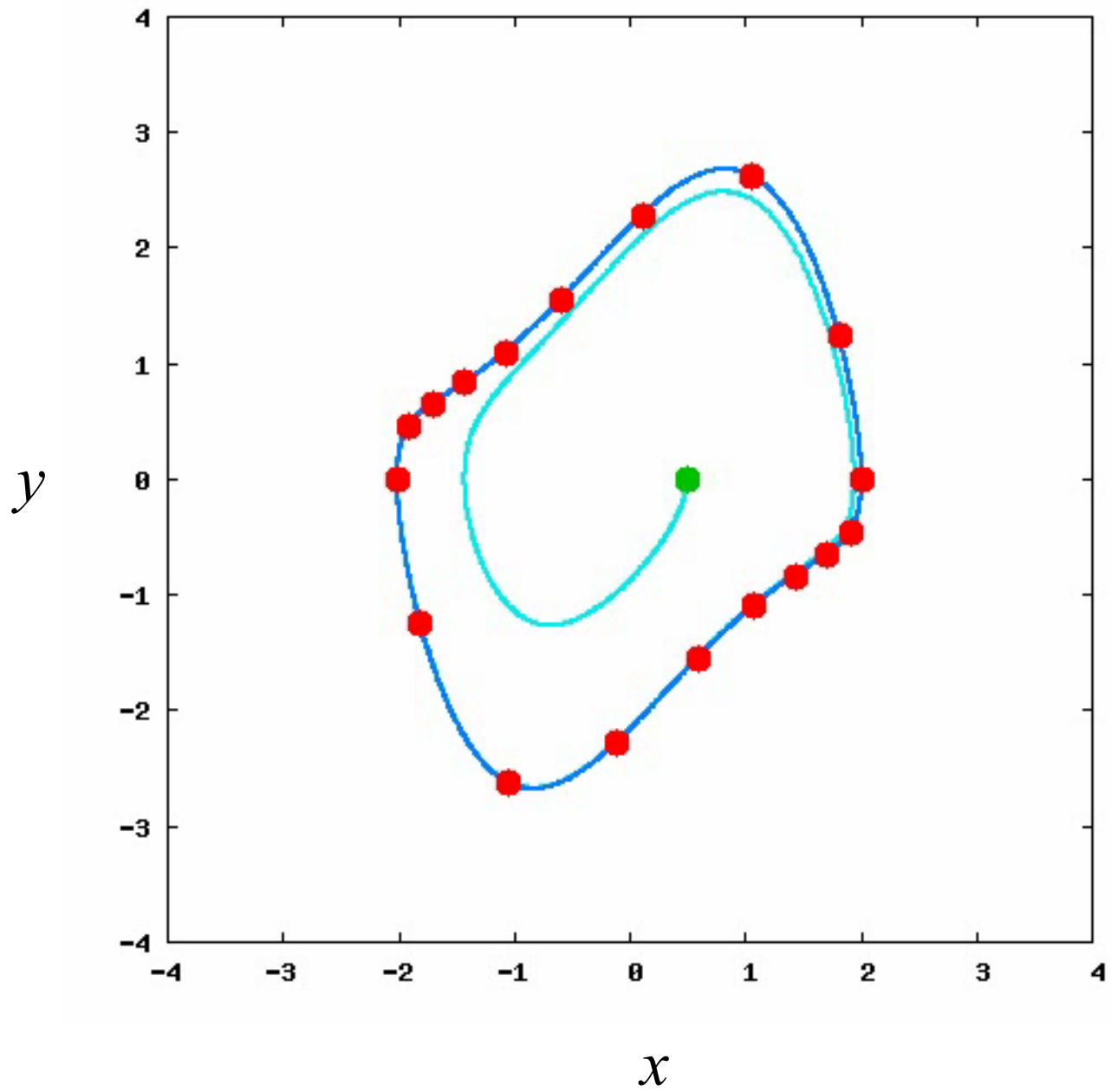
初期値を変えても



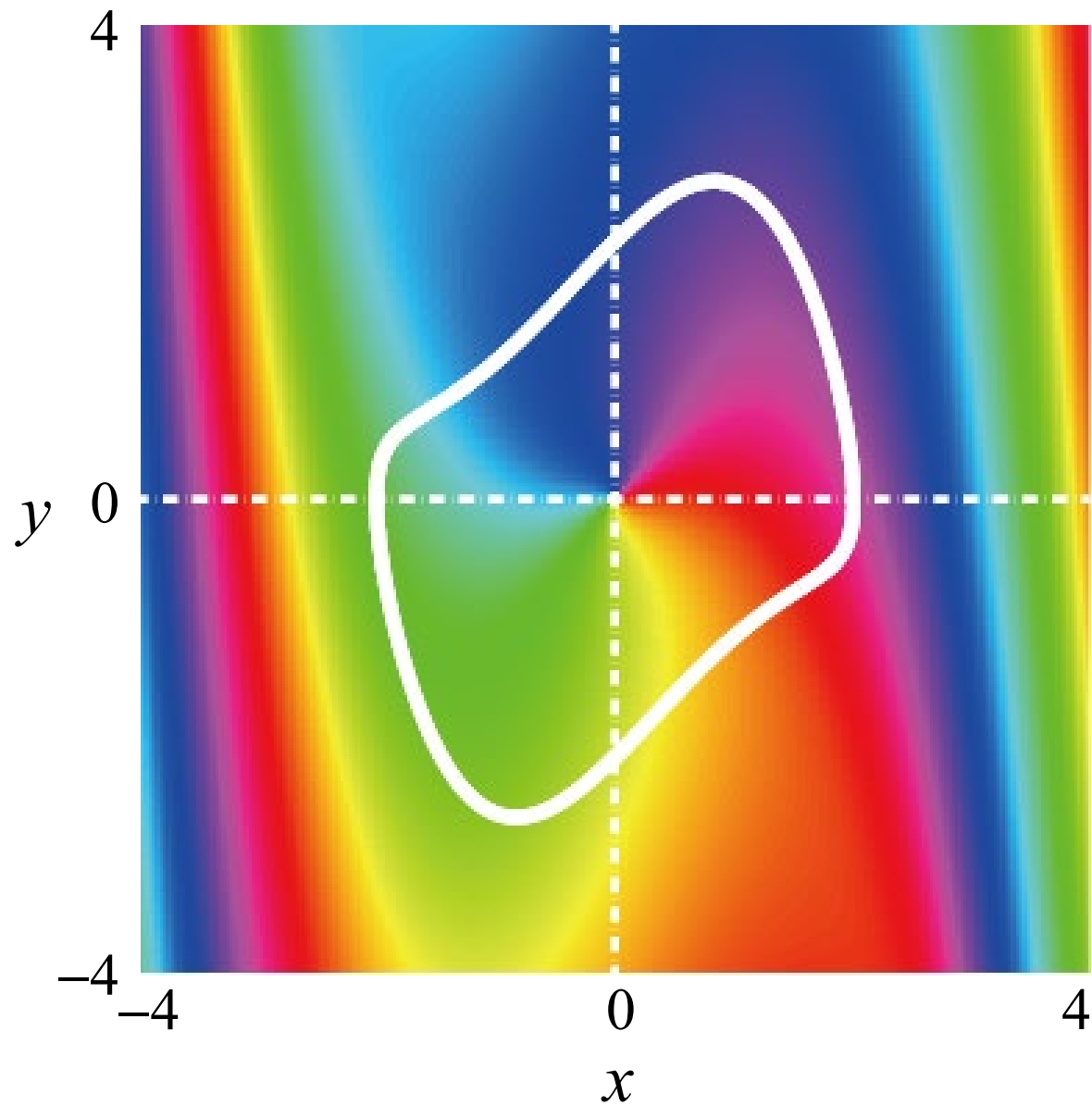
y



x



等位相面



Belousov-Zhabotinsky (BZ)反応の実験

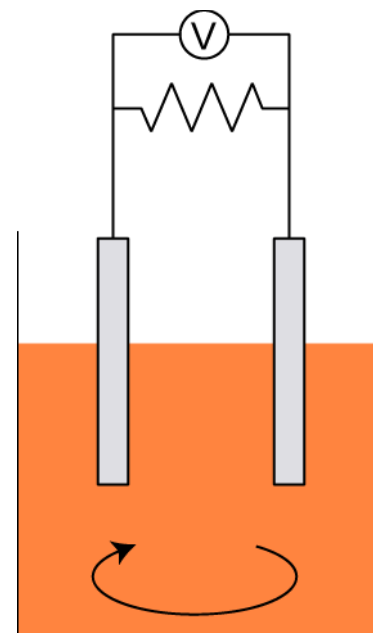
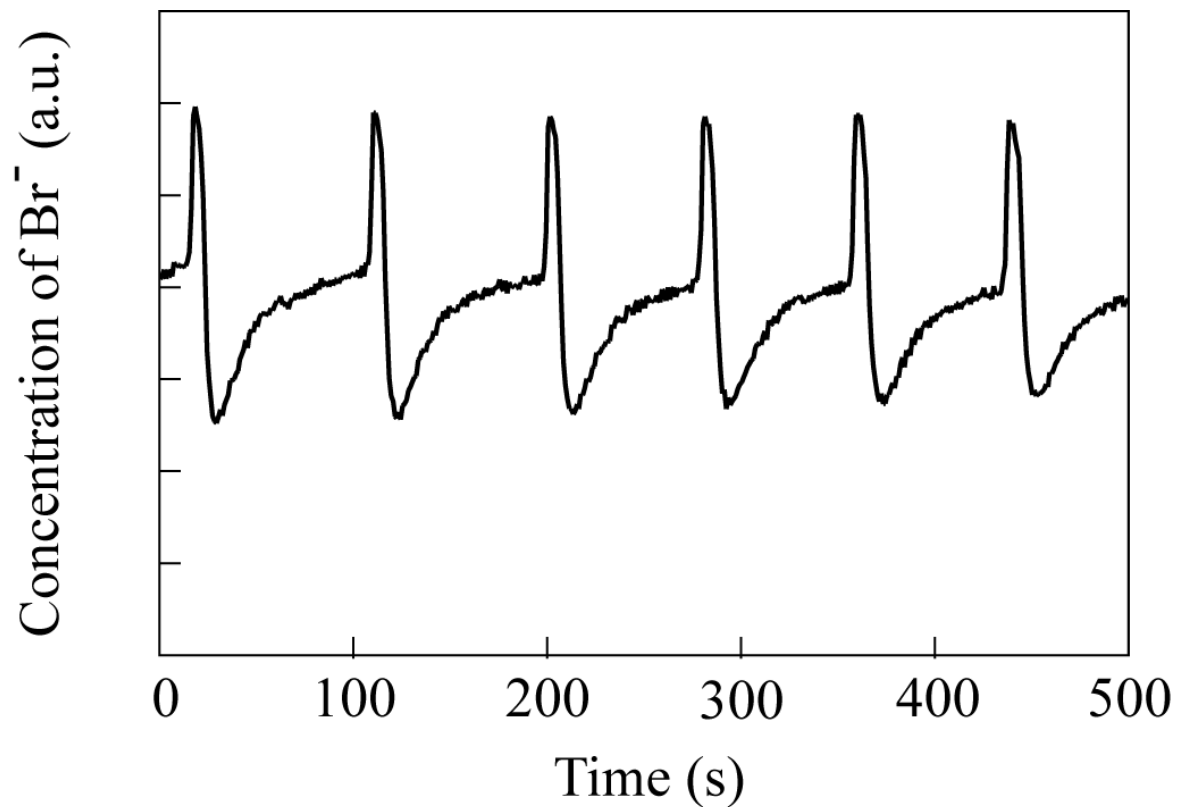
攪拌した系で



1 cm

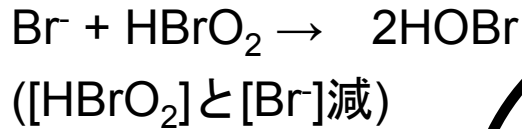
空間勾配はなし

電極を用いた臭化物イオン(Br^-)濃度の測定



BZ反応のメカニズム

Step I. [Br⁻]高の時

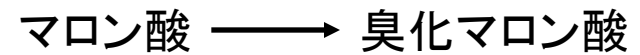


抑制因子(Br⁻)

Step III.

金属触媒の還元

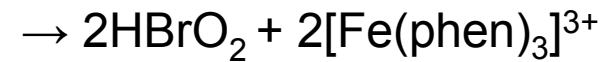
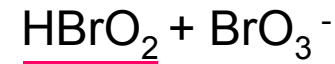
(臭化マロン酸とマロン酸による)



Step II. [Br⁻]低の時

金属触媒の酸化

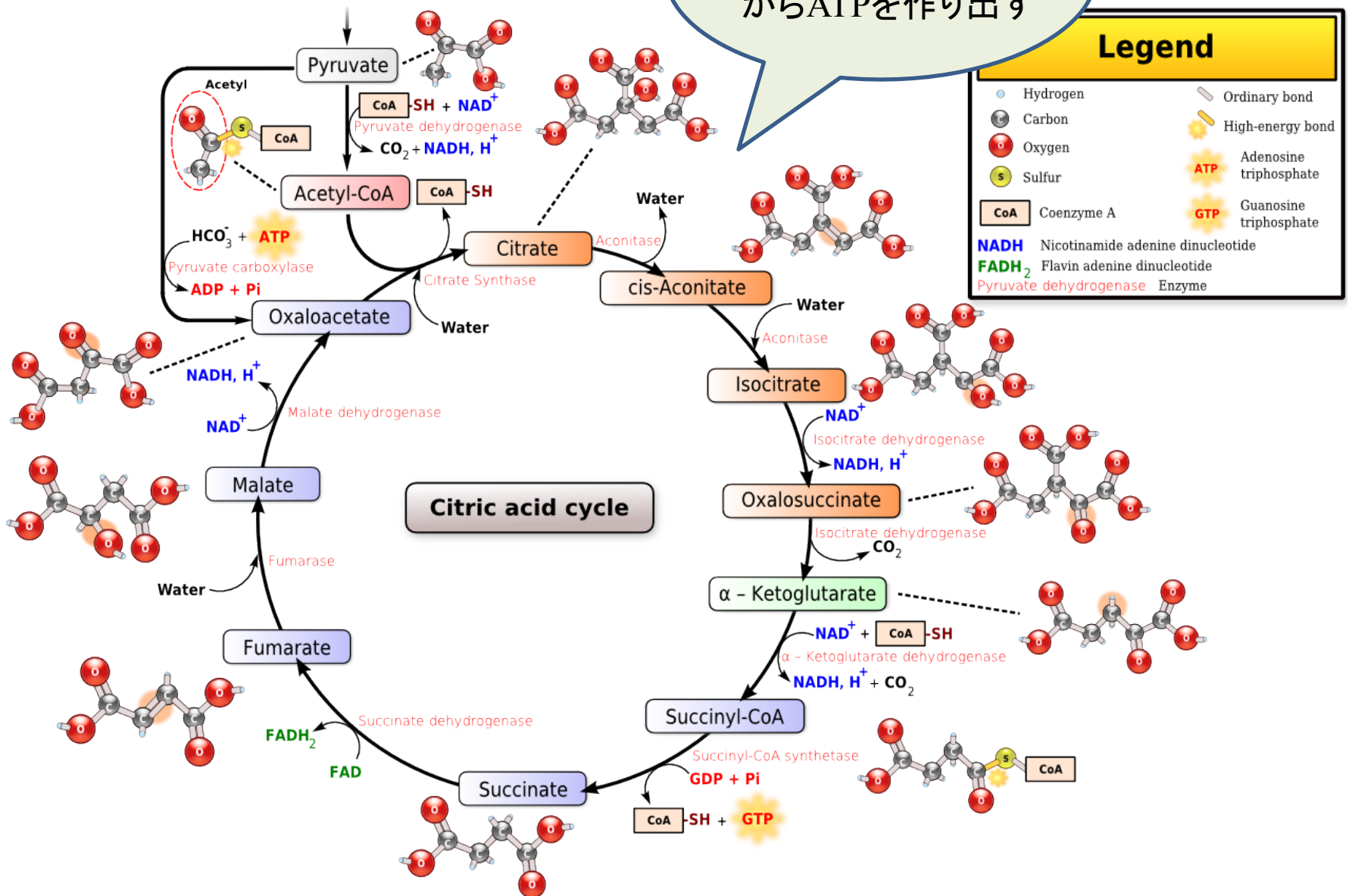
活性因子(HBrO₂)を自己触媒的に生成



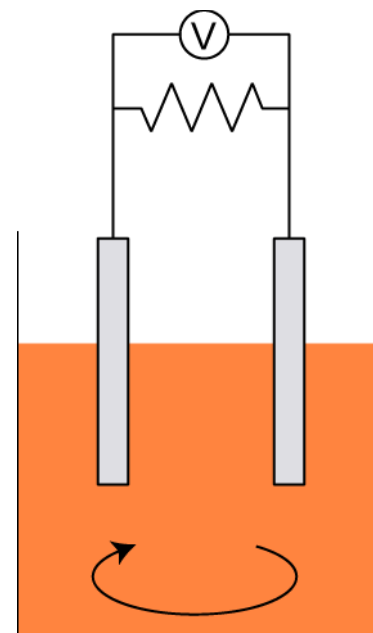
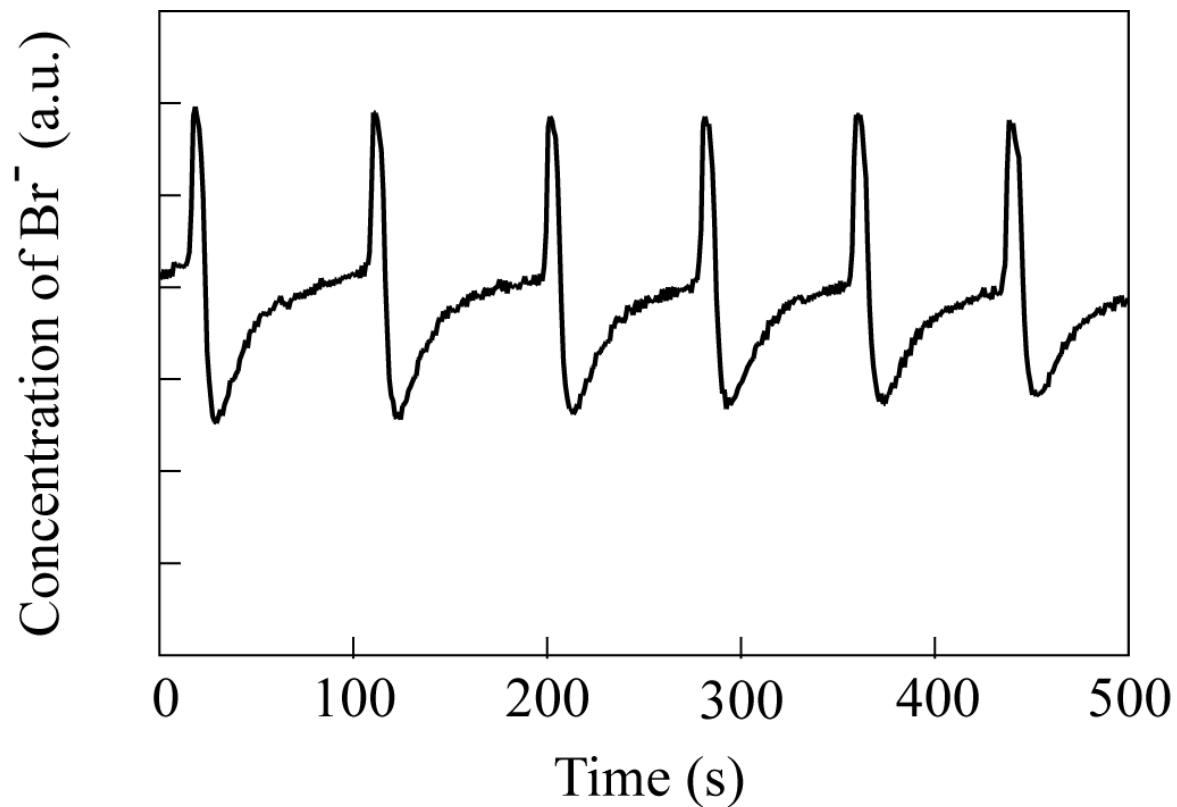
酸化反応 と 還元反応 が交互に起こる

クエン酸回路

ブドウ糖
(正確にはピルビン酸)
からATPを作り出す



電極を用いた臭化物イオン(Br^-)濃度の測定



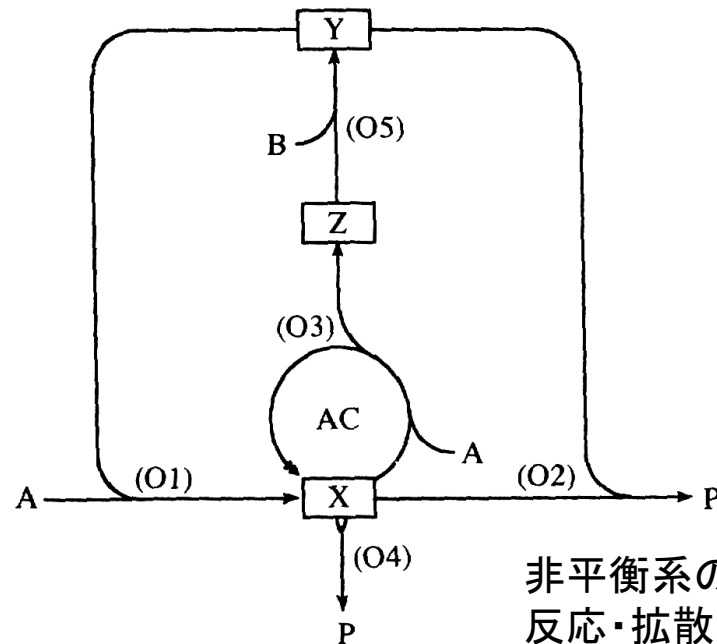
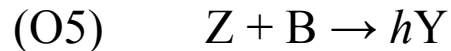
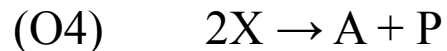
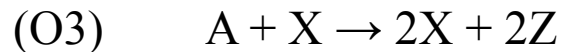
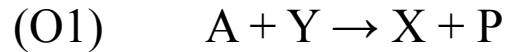
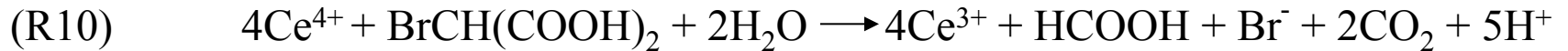
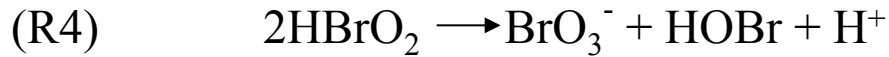
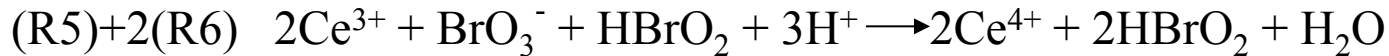
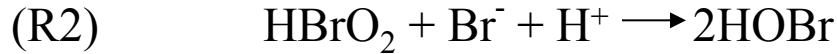
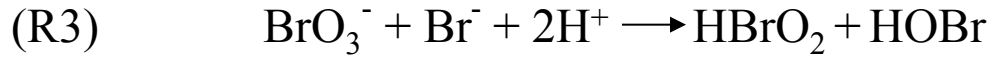
BZ反応のモデル化

FKN Model (R. J. Field, E. Körös, and R. M. Noyes, 1972).

化学反応の素過程から重要なものを抽出

- (R1) $\text{Br}^- + \text{HOBr} + \text{H}^+ \rightleftharpoons \text{Br}_2 + \text{H}_2\text{O}$
- (R2) $\text{Br}^- + \text{HBrO}_2 + \text{H}^+ \rightleftharpoons 2\text{HOBr}$
- (R3) $\text{Br}^- + \text{BrO}_3^- + 2\text{H}^+ \rightleftharpoons \text{HOBr} + \text{HBrO}_2$
- (R4) $2\text{HBrO}_2 \rightleftharpoons \text{HOBr} + \text{BrO}_3^- + \text{H}^+$
- (R5) $\text{HBrO}_2 + \text{BrO}_3^- + \text{H}^+ \rightleftharpoons 2\text{BrO}_2^\cdot + \text{H}_2\text{O}$
- (R6) $\text{BrO}_2^\cdot + \text{Ce}^{3+} + \text{H}^+ \rightleftharpoons \text{HBrO}_2 + \text{Ce}^{4+}$
- (R7) $\text{BrO}_2^\cdot + \text{Ce}^{4+} + \text{H}_2\text{O} \rightleftharpoons \text{BrO}_3^- + \text{Ce}^{3+} + 2\text{H}^+$
- (R8) $\text{Br}_2 + \text{CH}_2(\text{COOH})_2 \longrightarrow \text{BrCH}(\text{COOH})_2 + \text{Br}^- + \text{H}^+$
- (R9) $6\text{Ce}^{4+} + \text{CH}_2(\text{COOH})_2 + 2\text{H}_2\text{O} \longrightarrow 6\text{Ce}^{3+} + \text{HCOOH} + 3\text{CO}_2 + 6\text{H}^+$
- (R10) $4\text{Ce}^{4+} + \text{BrCH}(\text{COOH})_2 + 2\text{H}_2\text{O} \longrightarrow 4\text{Ce}^{3+} + \text{HCOOH} + \text{Br}^- + 2\text{CO}_2 + 5\text{H}^+$

3変数Oregonator (R. J. Field and R. M. Noyes, 1974).



非平衡系の科学III
 反応・拡散系のダイナミクス
 三池 秀敏ら 著

質量作用の法則より

$$\frac{dX}{dt} = k_3 H^2 A Y - k_2 H X Y + k_5 H A X - 2k_4 X^2$$

$$\frac{dY}{dt} = -k_3 H^2 A Y - k_2 H X Y + k_j B Z$$

$$\frac{dZ}{dt} = -2k_5 H A X - k_j B Z$$

化学反応には、速い反応と遅い反応がある。

速い反応は、すぐに平衡に達すると考えて、
近似することができる。

= 断熱消去



このとき、Nの濃度の時間変化はLの濃度のみによると考えることができる。

化学反応の素過程



FKN Model (R. J. Field, E. Körös, and R. M. Noyes, 1972).



3変数Oregonator (R. J. Field and R. M. Noyes, 1974).



2変数Oregonator (J. J. Tyson and P. C. Fife, 1980).

$$\begin{aligned}\frac{dU}{dt} &= f(U, V) \\ \frac{dV}{dt} &= g(U, V) \\ f(U, V) &= \frac{1}{\varepsilon} \left(U(1-U) - fV \frac{U-q}{U+q} \right) \\ g(U, V) &= U - V\end{aligned}$$

U : [HBrO₂]

V : [Fe(phen)₃³⁺]

青色

2変数Oregonator

(J. J. Tyson and P. C. Fife, 1980).

$$\frac{dU}{dt} = \frac{1}{\varepsilon} \left(U(1-U) - fV \frac{U-q}{U+q} \right)$$

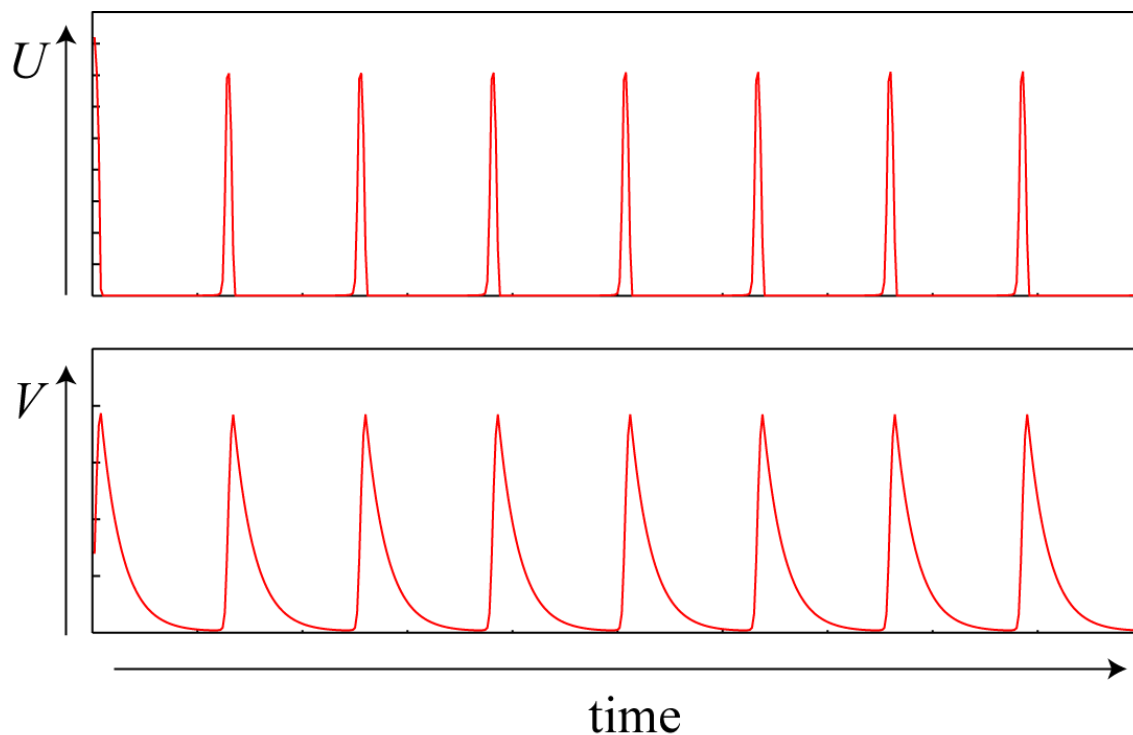
U : [HBrO₂]

V : [Fe(phen)₃³⁺]

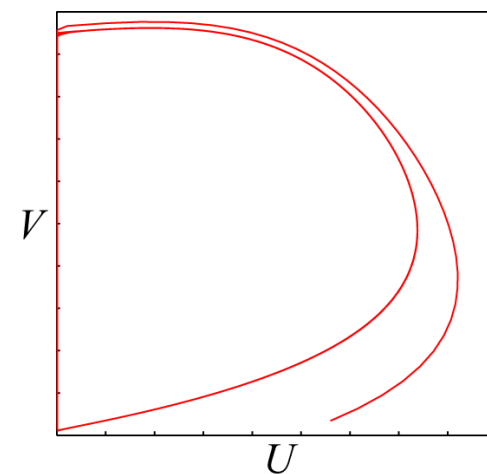
青色

$$\frac{dV}{dt} = U - V$$

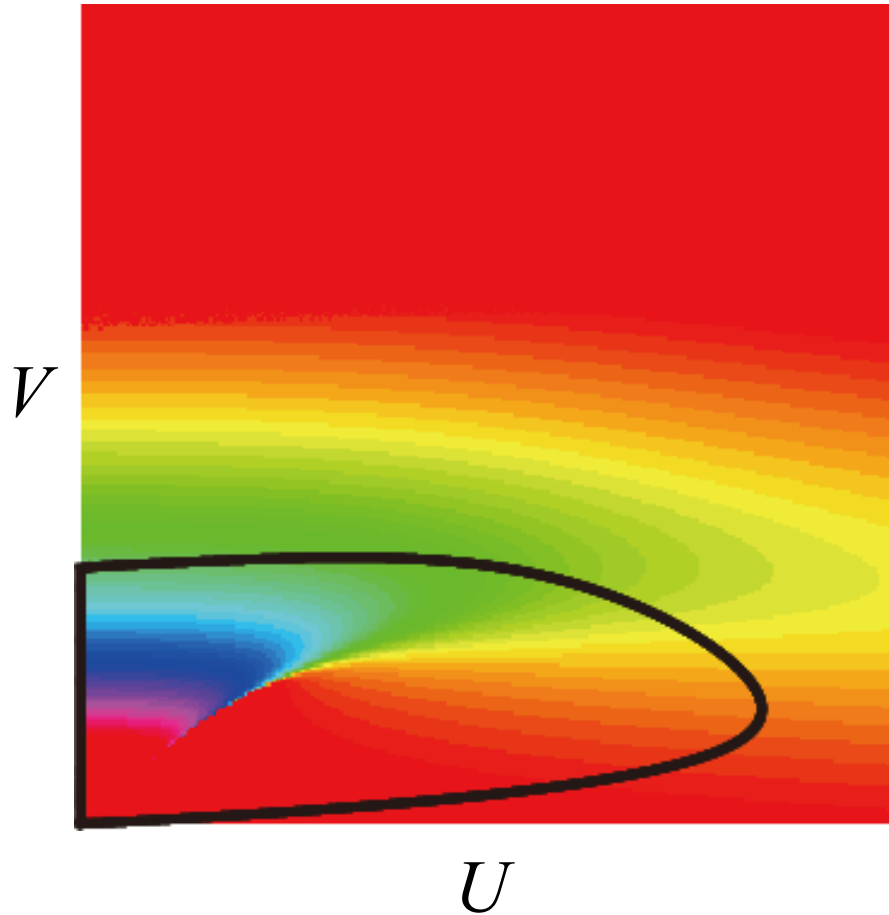
数値計算:



相平面で見ると

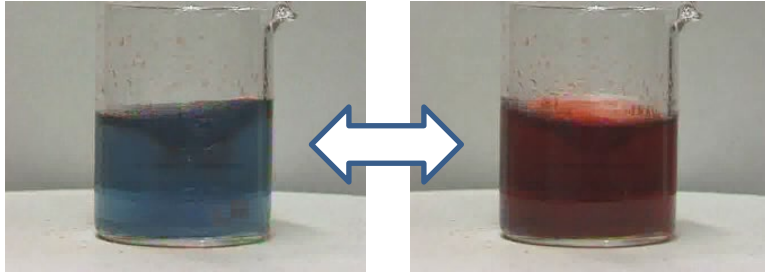


Oregonatorの等位相面



どちらもリミットサイクル振動なので、「位相」で考えられる。

具体(現象)から抽象(理論)へ



BZ反応

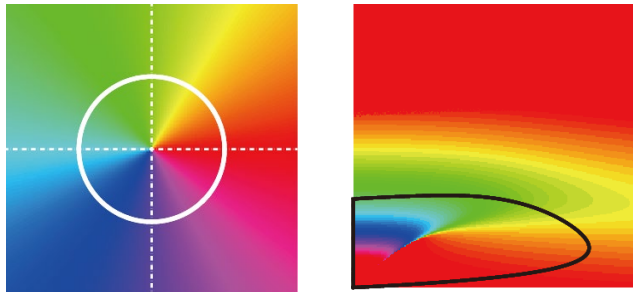
化学反応式 (物質に近いモデル)

- (R1) $\text{Br}^- + \text{HOBr} + \text{H}^+ \rightleftharpoons \text{Br}_2 + \text{H}_2\text{O}$
- (R2) $\text{Br}^- + \text{HBrO}_2 + \text{H}^+ \rightleftharpoons 2\text{HOBr}$
- (R3) $\text{Br}^- + \text{BrO}_3^- + 2\text{H}^+ \rightleftharpoons \text{HOBr} + \text{HBrO}_2$
- (R4) $2\text{HBrO}_2 \rightleftharpoons \text{HOBr} + \text{BrO}_3^- + \text{H}^+$
- (R5) $\text{HBrO}_2 + \text{BrO}_3^- + \text{H}^+ \rightleftharpoons 2\text{BrO}_2 \cdot + \text{H}_2\text{O}$
- (R6) $\text{BrO}_2 \cdot + \text{Ce}^{4+} + \text{H}^+ \rightleftharpoons \text{HBrO}_2 + \text{Ce}^{4+}$
- (R7) $\text{BrO}_2 \cdot + \text{Ce}^{4+} + \text{H}_2\text{O} \rightleftharpoons \text{BrO}_3^- + \text{Ce}^{3+} + 2\text{H}^+$
- (R8) $\text{Br}_2 + \text{CH}_2(\text{COOH})_2 \rightarrow \text{BrCH}(\text{COOH})_2 + \text{Br}^- + \text{H}^+$
- (R9) $6\text{Ce}^{4+} + \text{CH}_2(\text{COOH})_2 + 2\text{H}_2\text{O} \rightarrow 6\text{Ce}^{3+} + \text{HCOOH} + 3\text{CO}_2 + 6\text{H}^+$
- (R10) $4\text{Ce}^{4+} + \text{BrCH}(\text{COOH})_2 + 2\text{H}_2\text{O} \rightarrow 4\text{Ce}^{3+} + \text{HCOOH} + \text{Br}^- + 2\text{CO}_2 + 5\text{H}^+$



Stuart-Landau方程式 (位相記述・分岐理論)

Oregonator (断熱近似・無次元化)



$$\frac{dU}{dt} = f(U, V)$$

$$\frac{dV}{dt} = g(U, V)$$

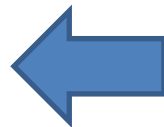
$$f(U, V) = \frac{1}{\varepsilon} \left(U(1-U) - fV \frac{U-q}{U+q} \right)$$

$$g(U, V) = U - V$$

U : $[\text{HBrO}_2]$

V : $[\text{Fe}(\text{phen})_3^{3+}]$

青色



実験室で見られる時空間秩序形成

さまざまなリズム現象

Briggs Rauscher (BR)
reaction



candle oscillator



x15/100 speed

camphor crystallization



real time

2 mm

HK JPCA 2009

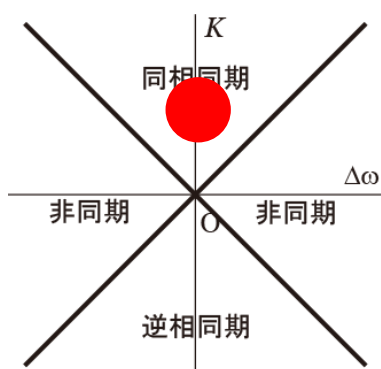
Sasaki JPCB 2015

非線形振動子の結合系

非線形振動子の結合系

2振動子の結合系

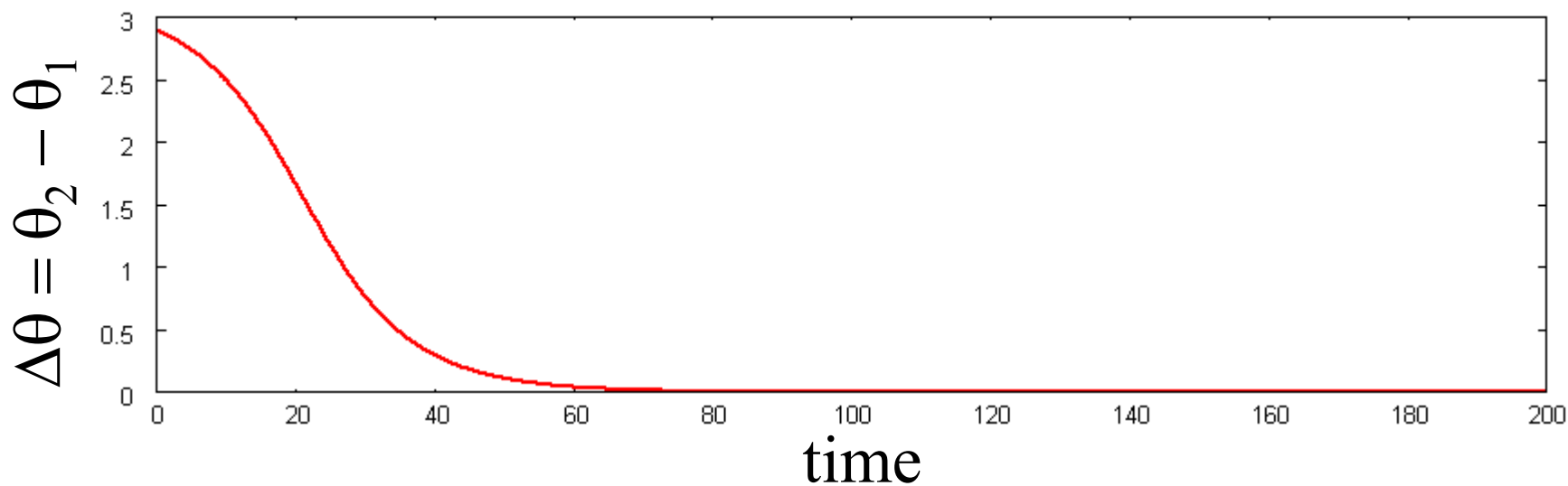
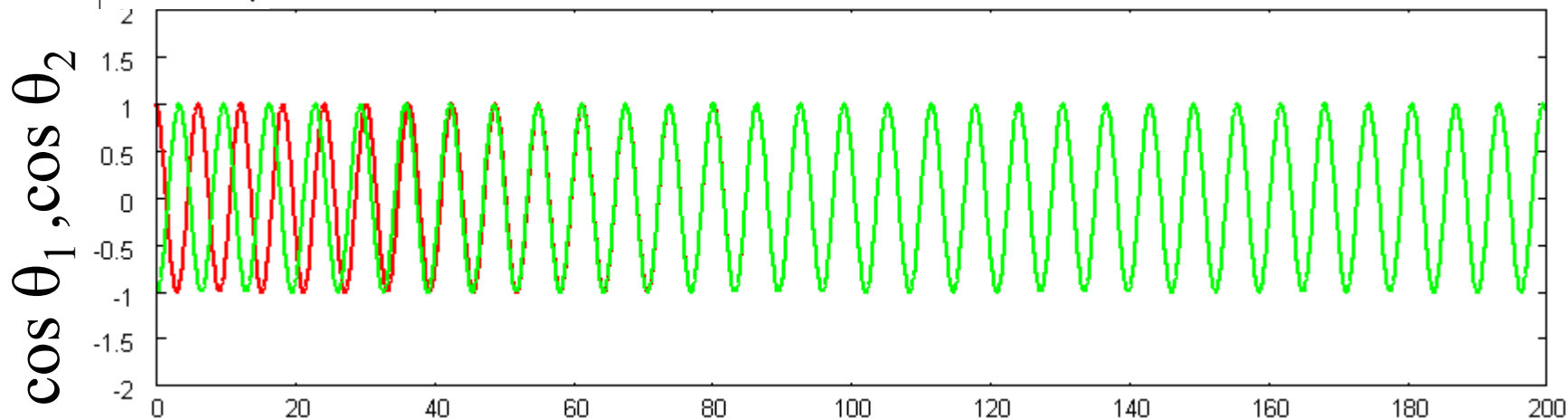
$$\left\{ \begin{array}{l} \frac{d\theta_1}{dt} = \omega_1 + K \sin(\theta_2 - \theta_1) \\ \frac{d\theta_2}{dt} = \omega_2 + K \sin(\theta_1 - \theta_2) \end{array} \right.$$

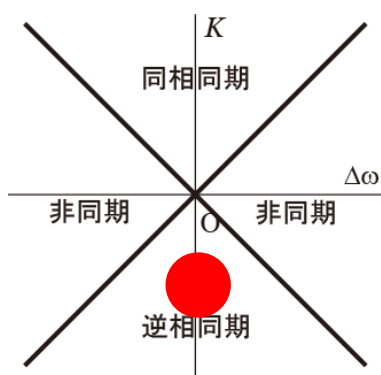


$$\begin{cases} \frac{d\theta_1}{dt} = \omega_1 + K \sin(\theta_2 - \theta_1) \\ \frac{d\theta_2}{dt} = \omega_2 + K \sin(\theta_1 - \theta_2) \end{cases}$$

$$\omega_1 = \omega_2 = 1$$

$$K = 0.05$$

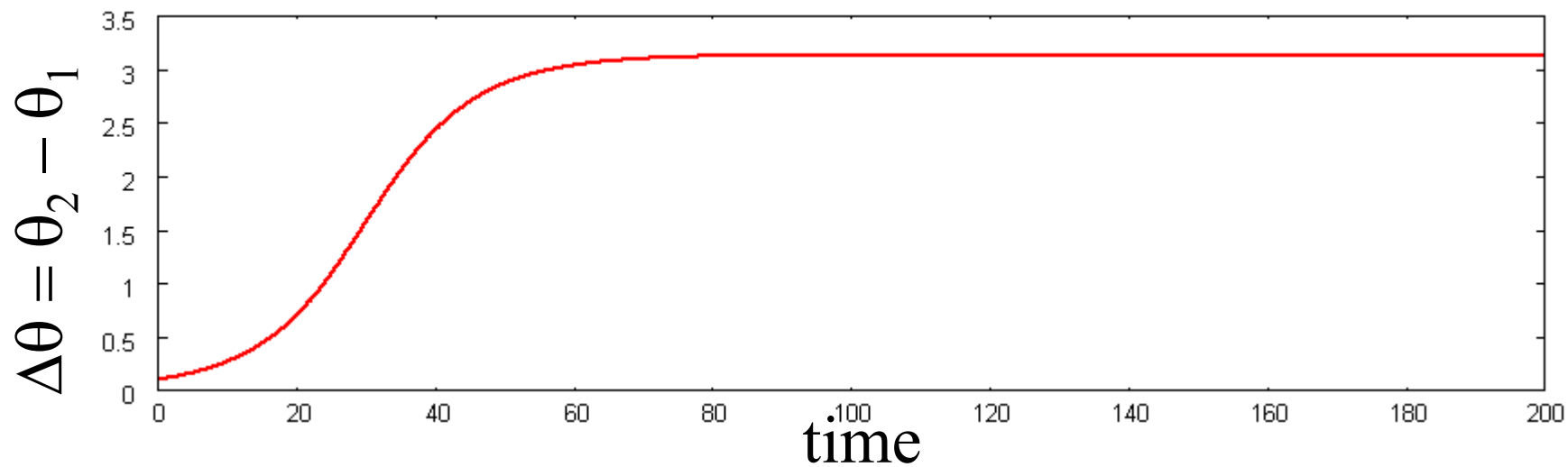
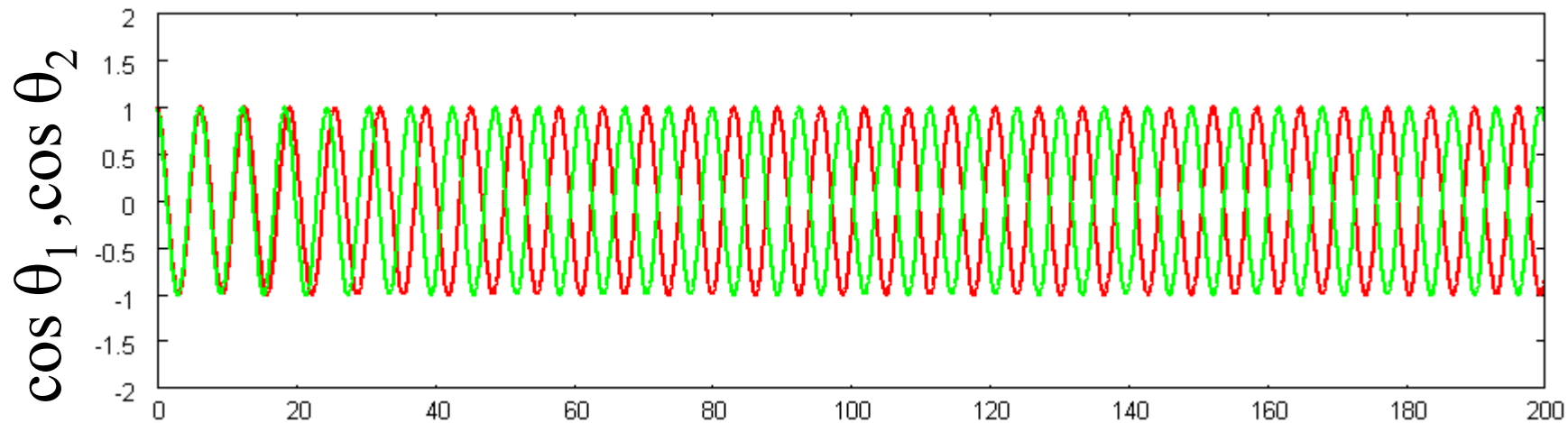


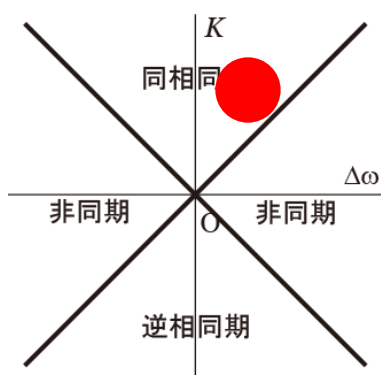


$$\begin{cases} \frac{d\theta_1}{dt} = \omega_1 + K \sin(\theta_2 - \theta_1) \\ \frac{d\theta_2}{dt} = \omega_2 + K \sin(\theta_1 - \theta_2) \end{cases}$$

$$\omega_1 = \omega_2 = 1$$

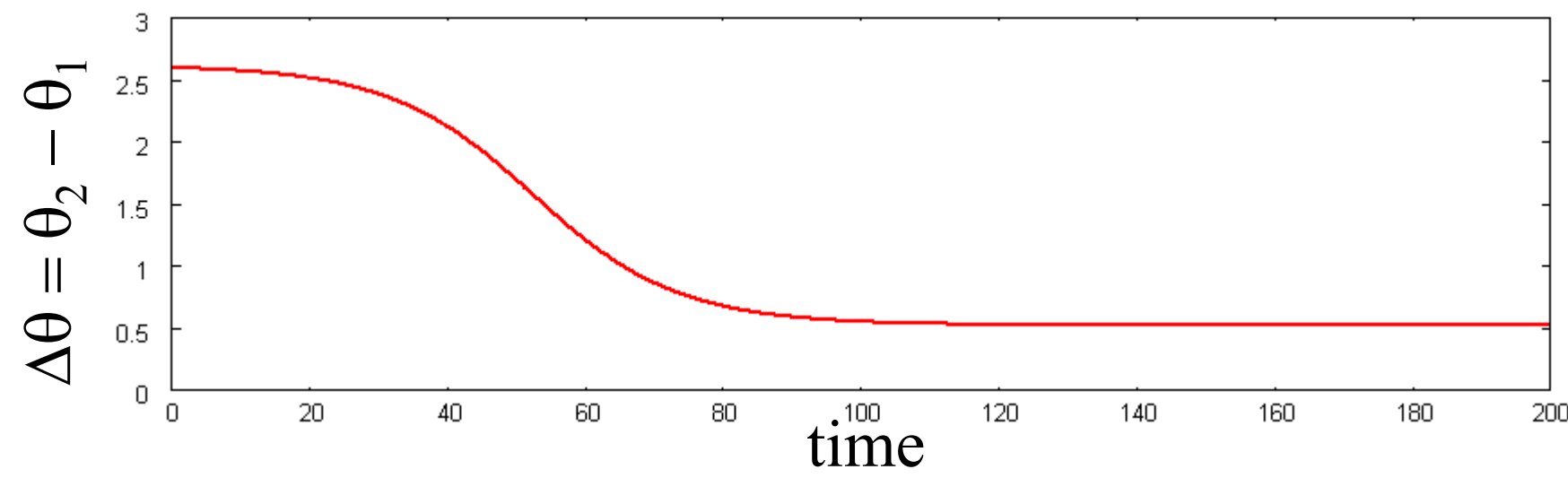
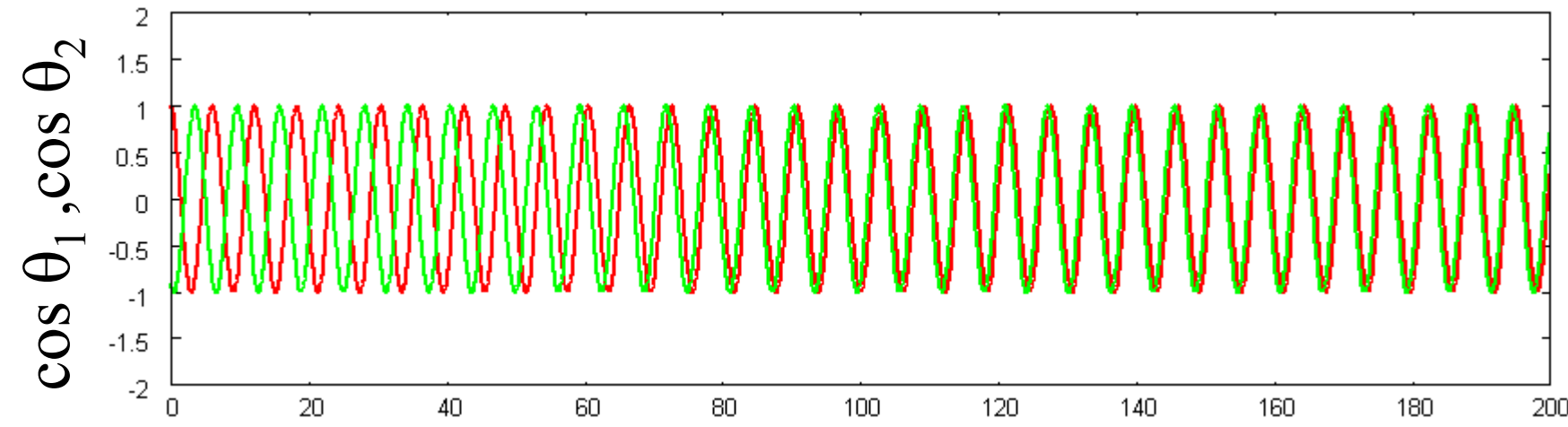
$$K = -0.05$$

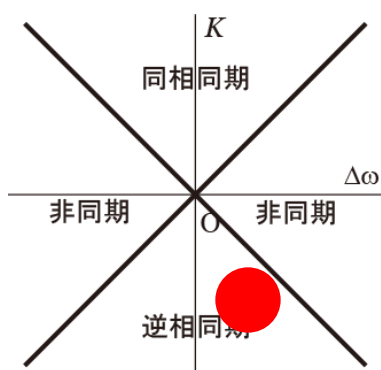




$$\begin{cases} \frac{d\theta_1}{dt} = \omega_1 + K \sin(\theta_2 - \theta_1) \\ \frac{d\theta_2}{dt} = \omega_2 + K \sin(\theta_1 - \theta_2) \end{cases}$$

$$\begin{aligned} \omega_1 &= 1, \quad \omega_2 = 1.05 \\ K &= 0.05 \end{aligned}$$

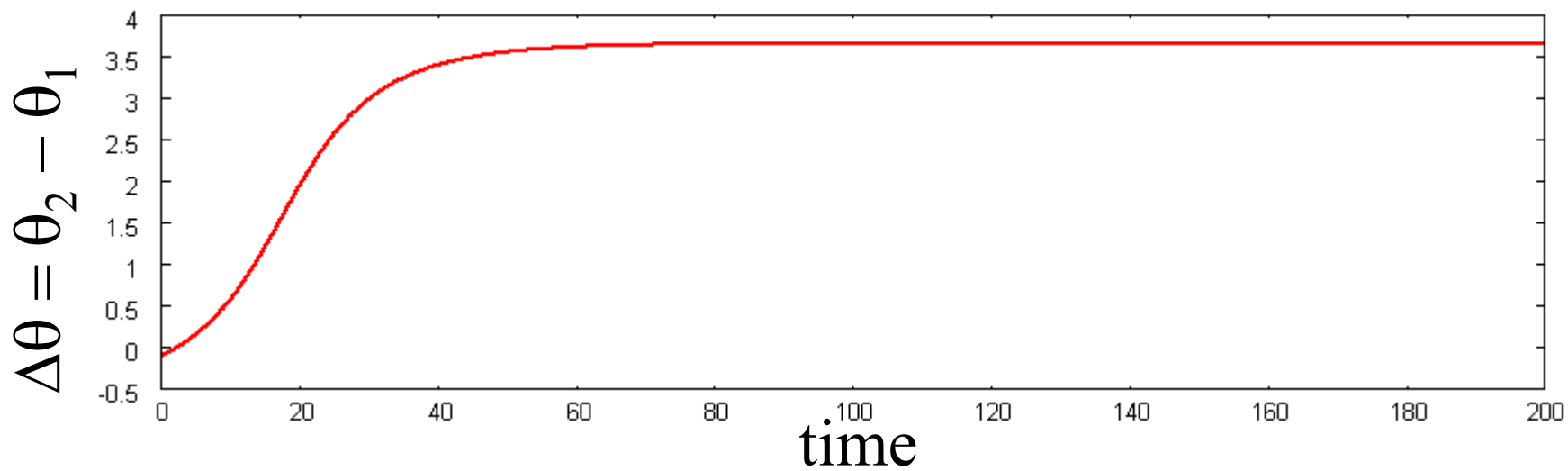
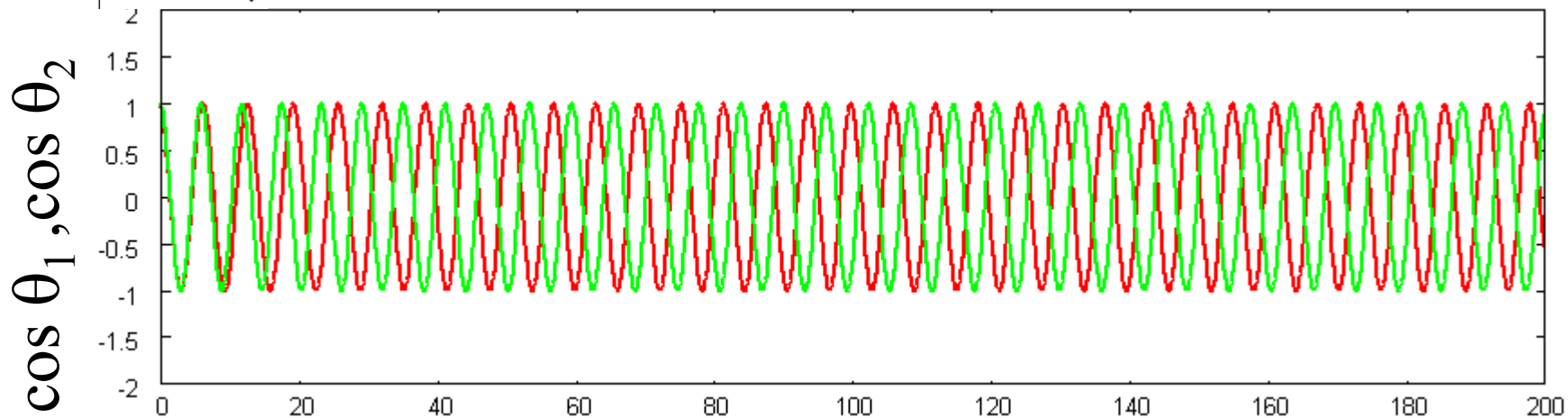


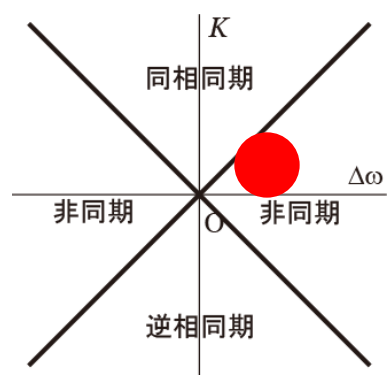


$$\begin{cases} \frac{d\theta_1}{dt} = \omega_1 + K \sin(\theta_2 - \theta_1) \\ \frac{d\theta_2}{dt} = \omega_2 + K \sin(\theta_1 - \theta_2) \end{cases}$$

$$\omega_1 = 1, \omega_2 = 1.05$$

$$K = -0.05$$

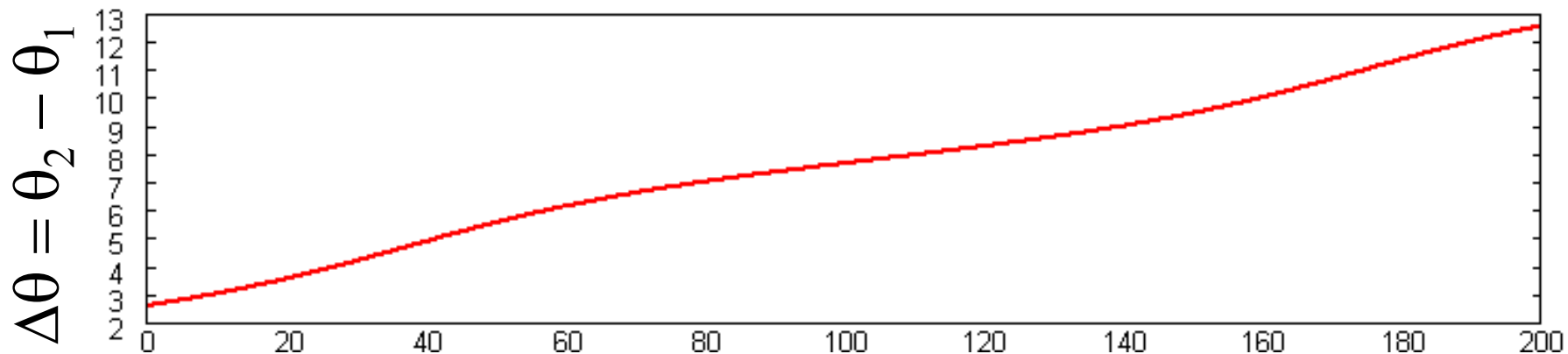
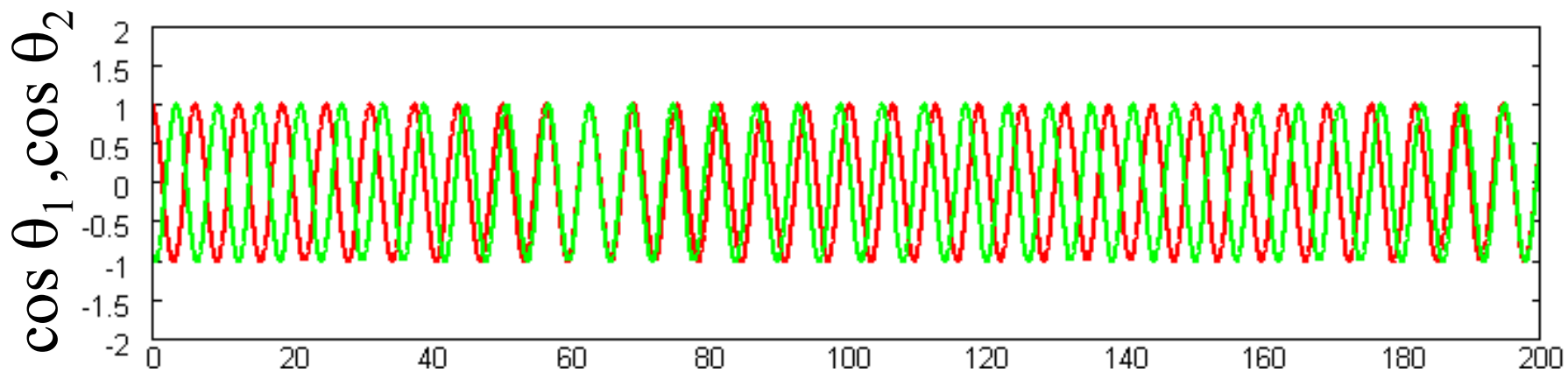




$$\begin{cases} \frac{d\theta_1}{dt} = \omega_1 + K \sin(\theta_2 - \theta_1) \\ \frac{d\theta_2}{dt} = \omega_2 + K \sin(\theta_1 - \theta_2) \end{cases}$$

$$\omega_1 = 1, \omega_2 = 1.05$$

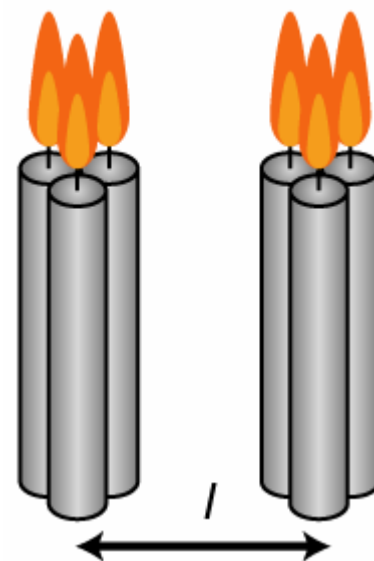
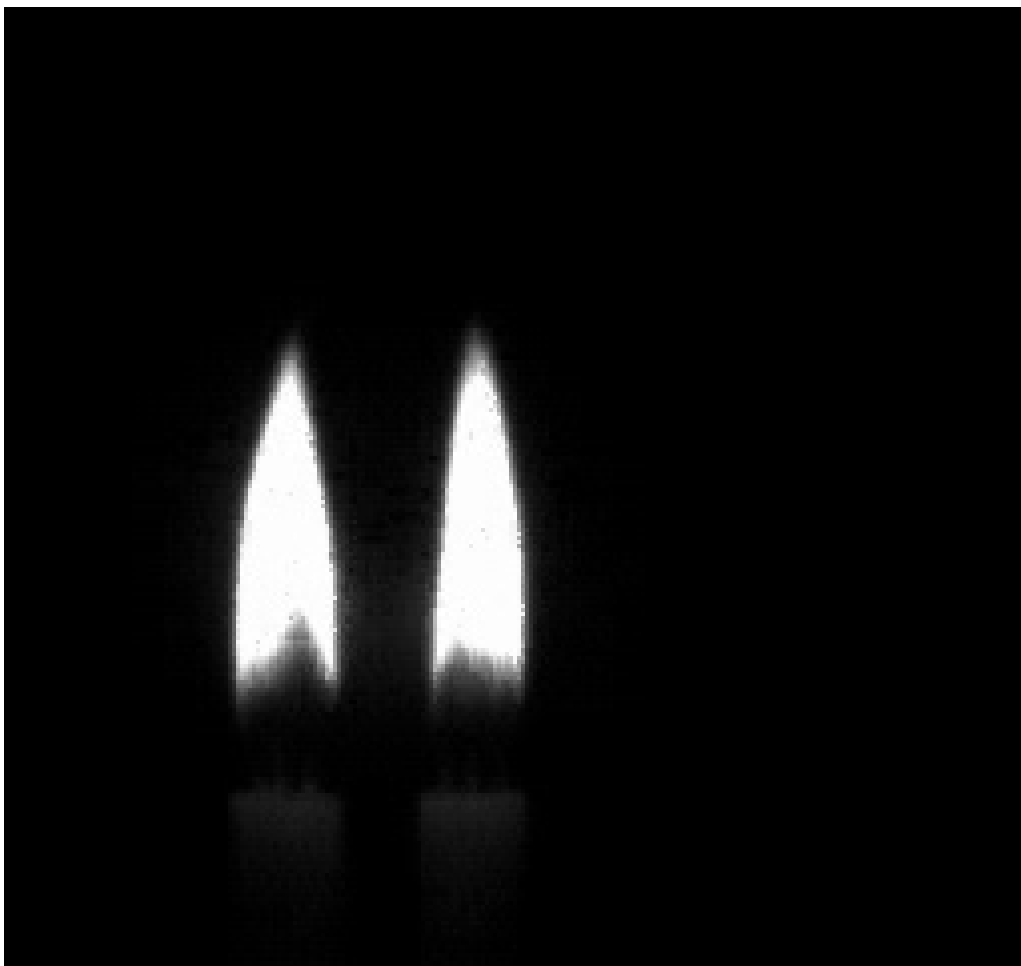
$$K = 0.01$$



time

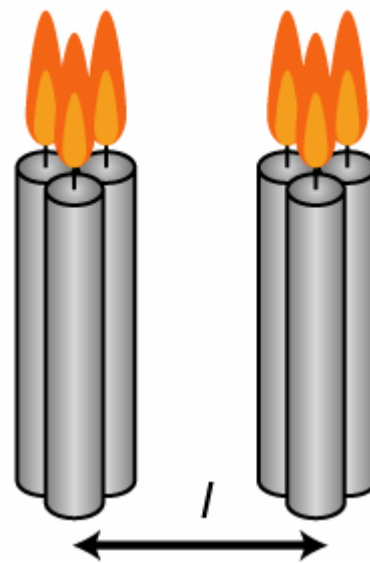
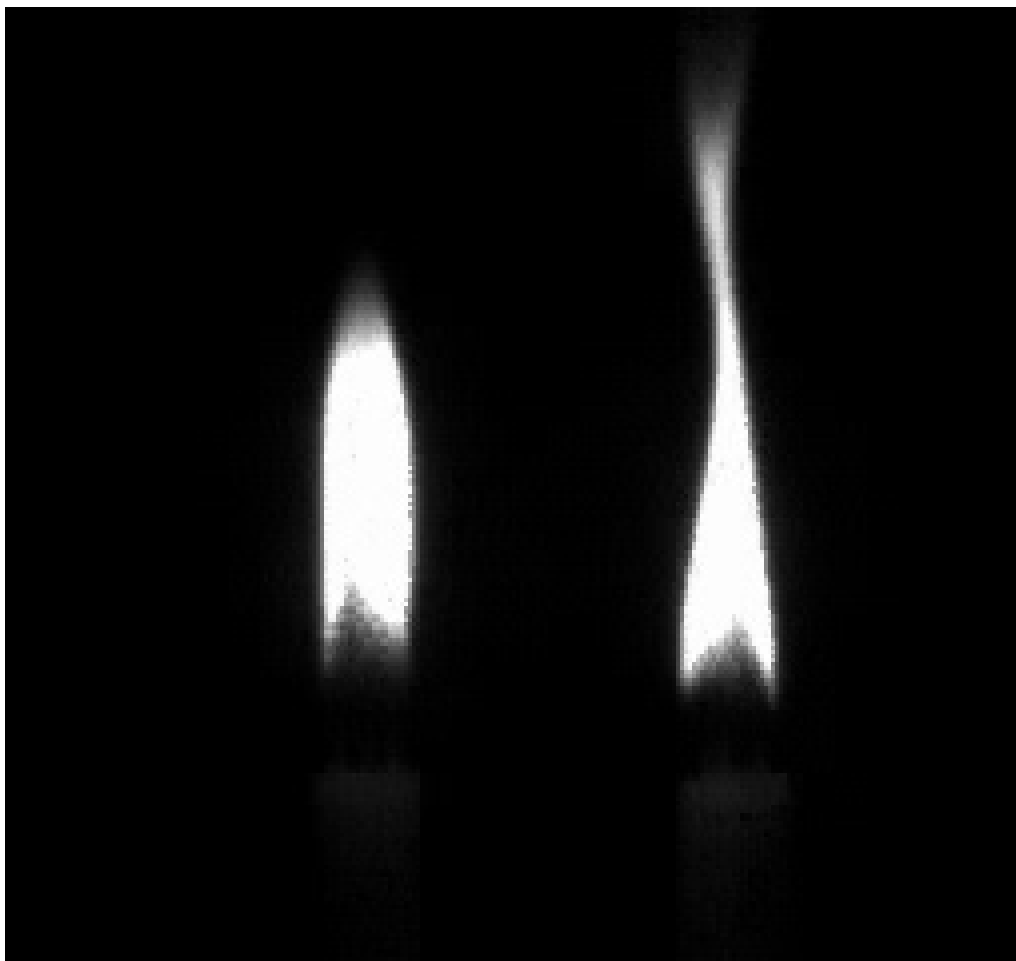
ろうそく振動子

$l = 2.0 \text{ mm}$



15/100 times fast

$l = 4.0 \text{ mm}$



15/100 times fast

HK et al., *J. Phys. Chem. A* (2009).