

2009.12.15

物性物理学C

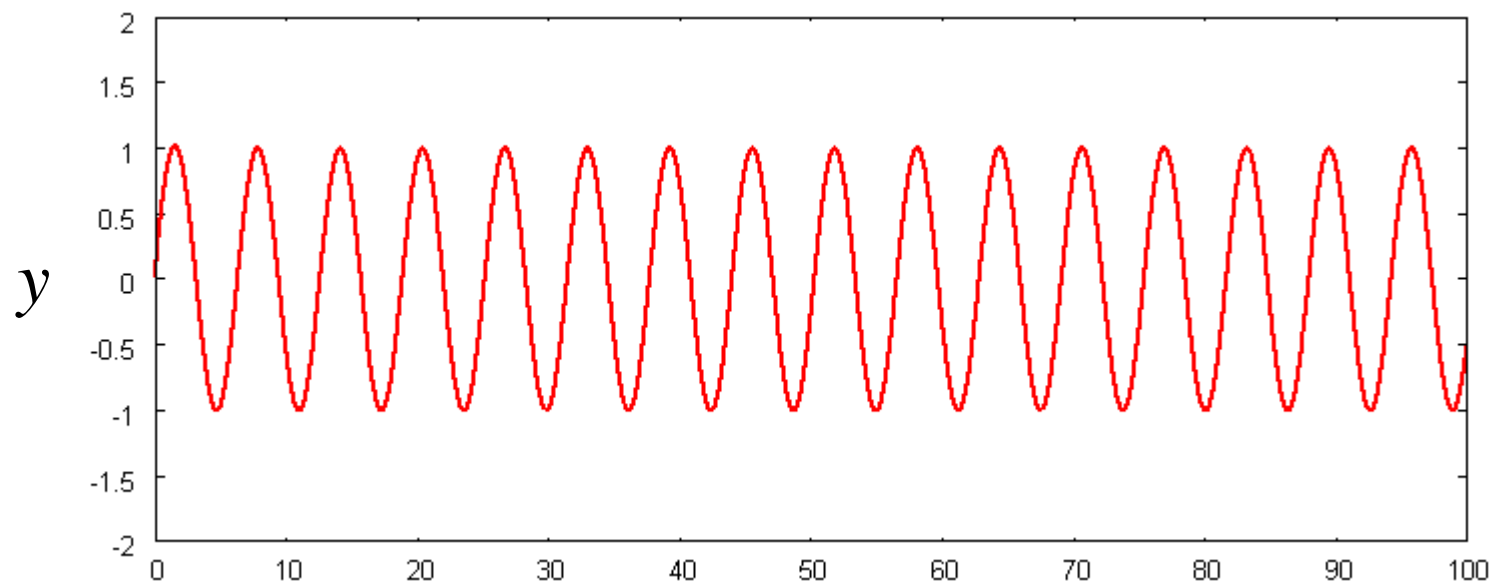
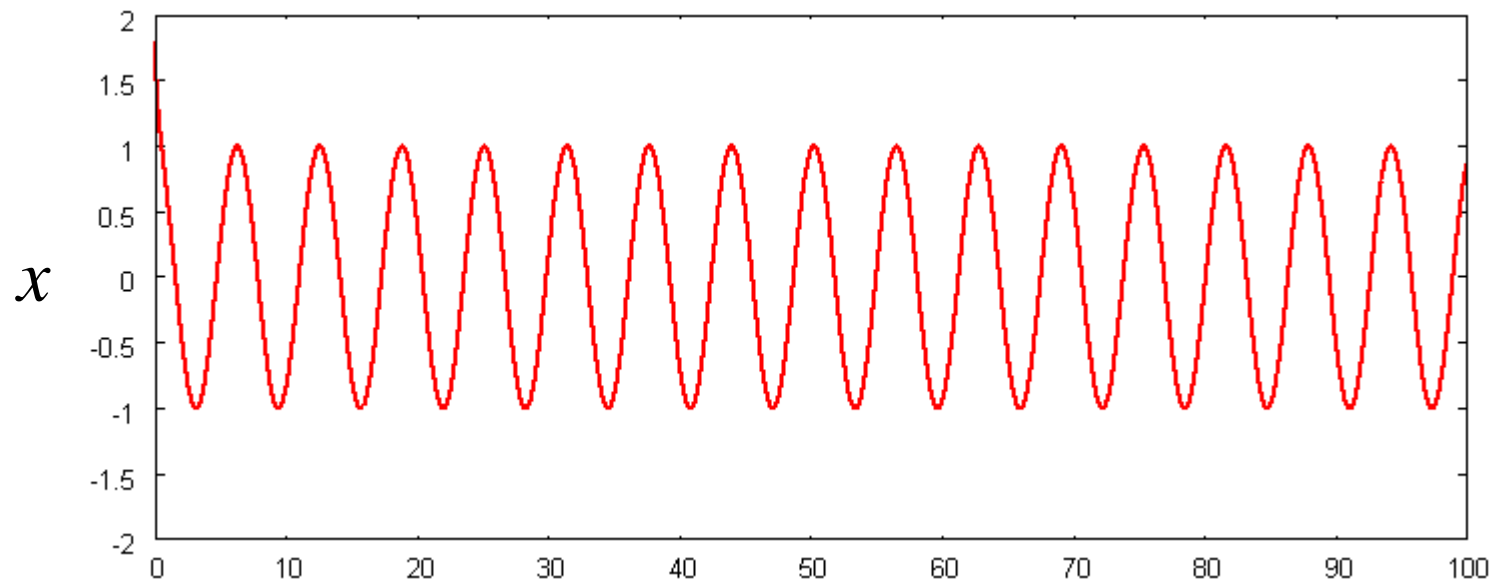
非線形振動子と同期現象

北畑 裕之

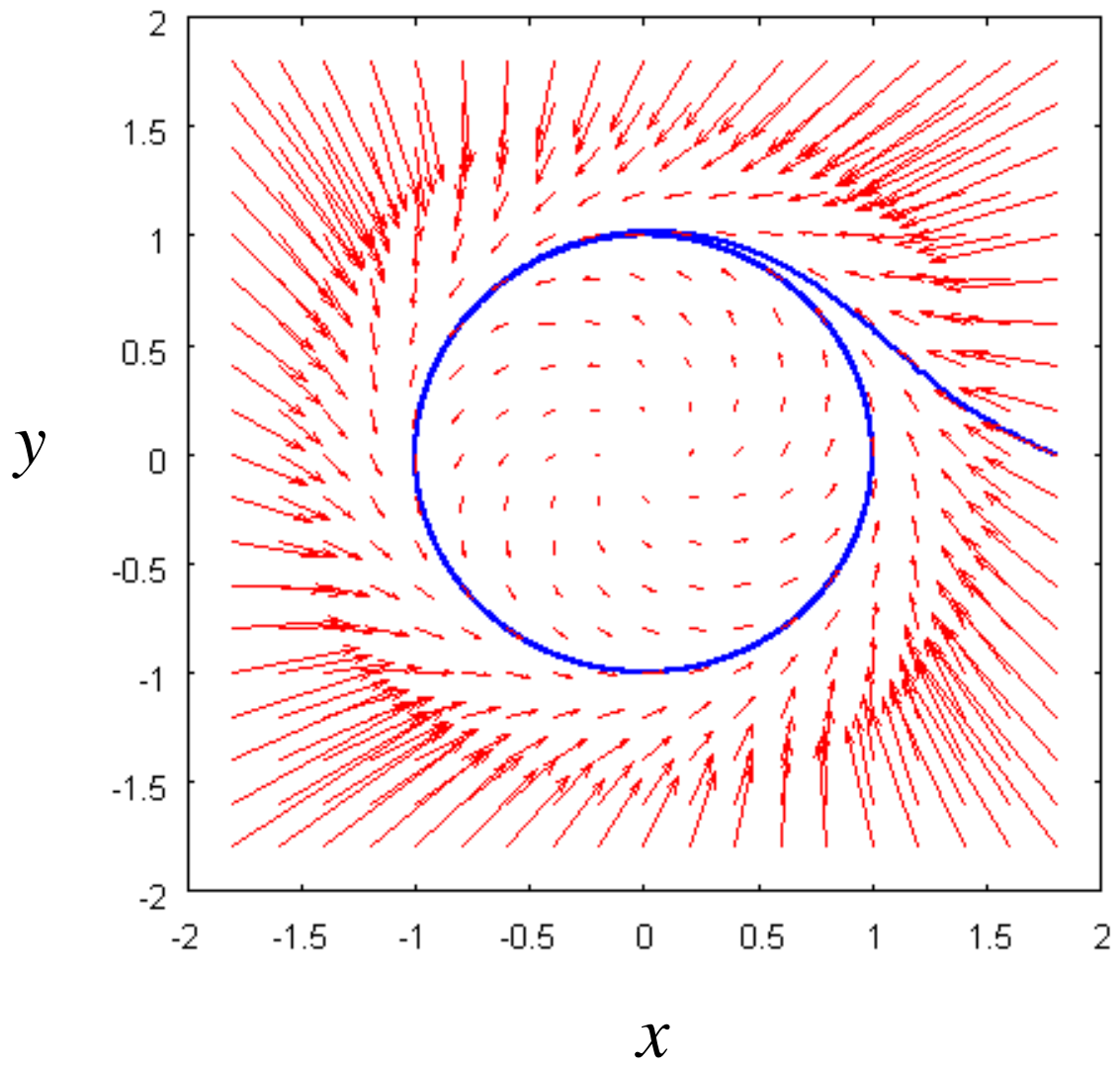
Stuart-Landau方程式

$$\begin{cases} \frac{dx}{dt} = ax - \omega y - (x^2 + y^2)(x - by) \\ \frac{dy}{dt} = ay + \omega x - (x^2 + y^2)(y + bx) \end{cases}$$

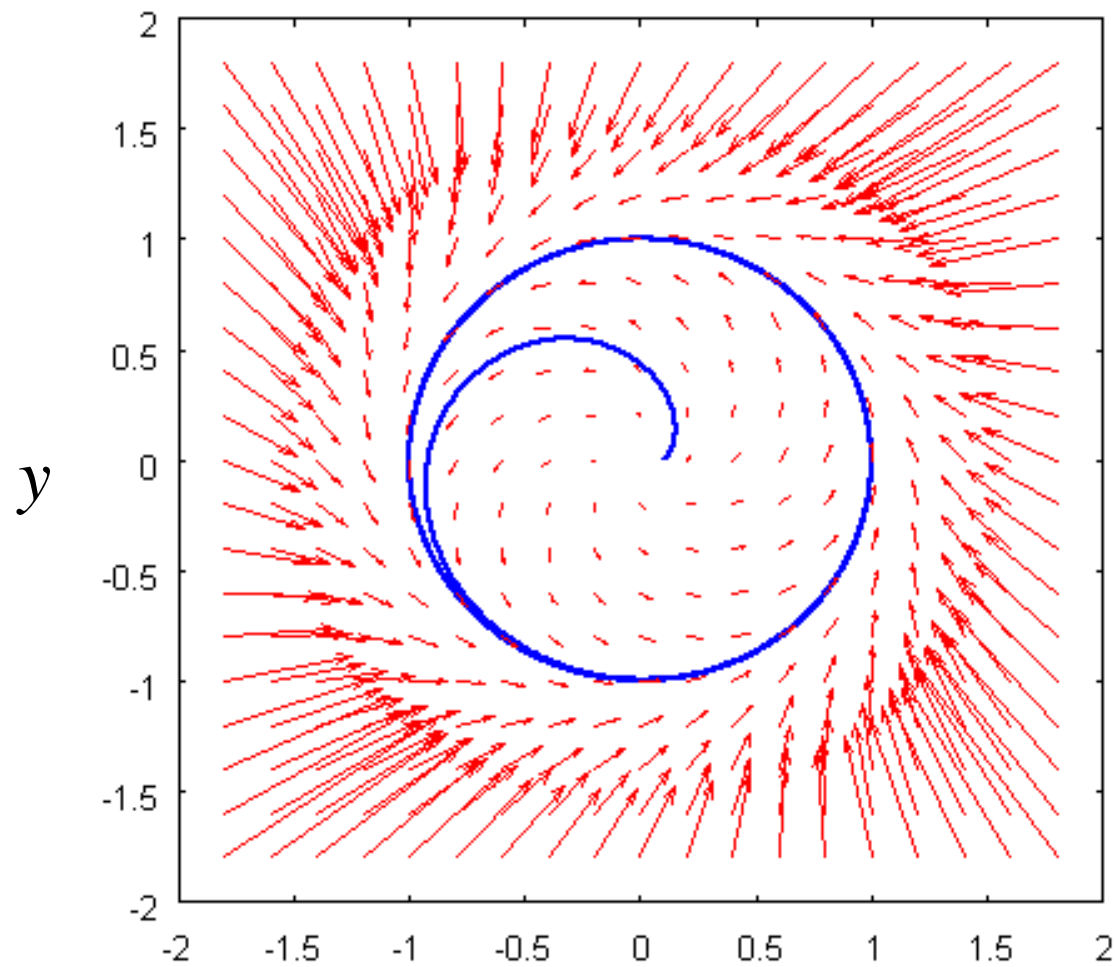
$$\begin{cases} \frac{dr}{dt} = ar - r^3 & r^2 = x^2 + y^2 & a = 1 \\ \frac{d\theta}{dt} = \omega & \frac{y}{x} = \tan \theta & b = 0 \end{cases}$$



time



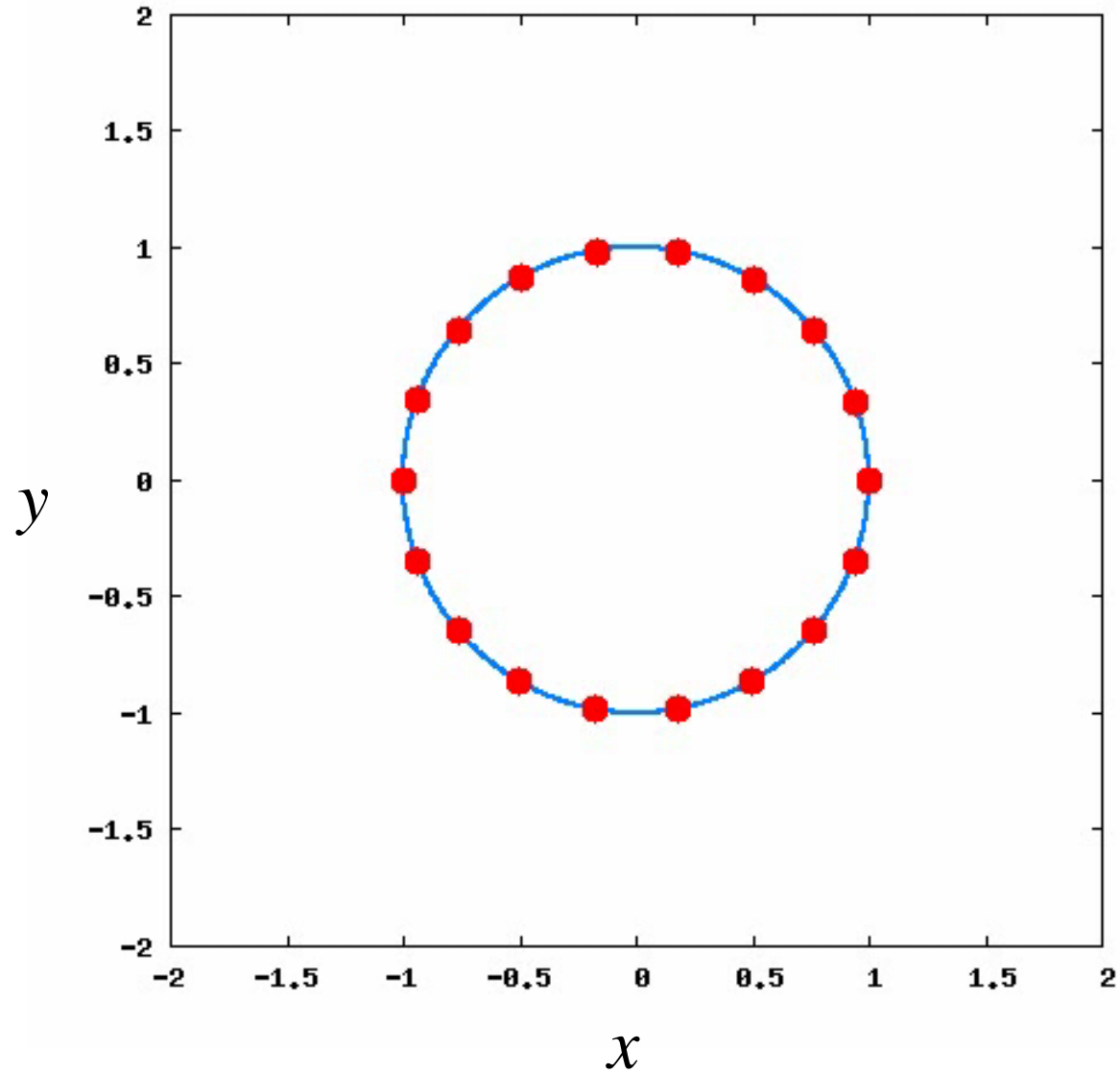
初期値を変えても

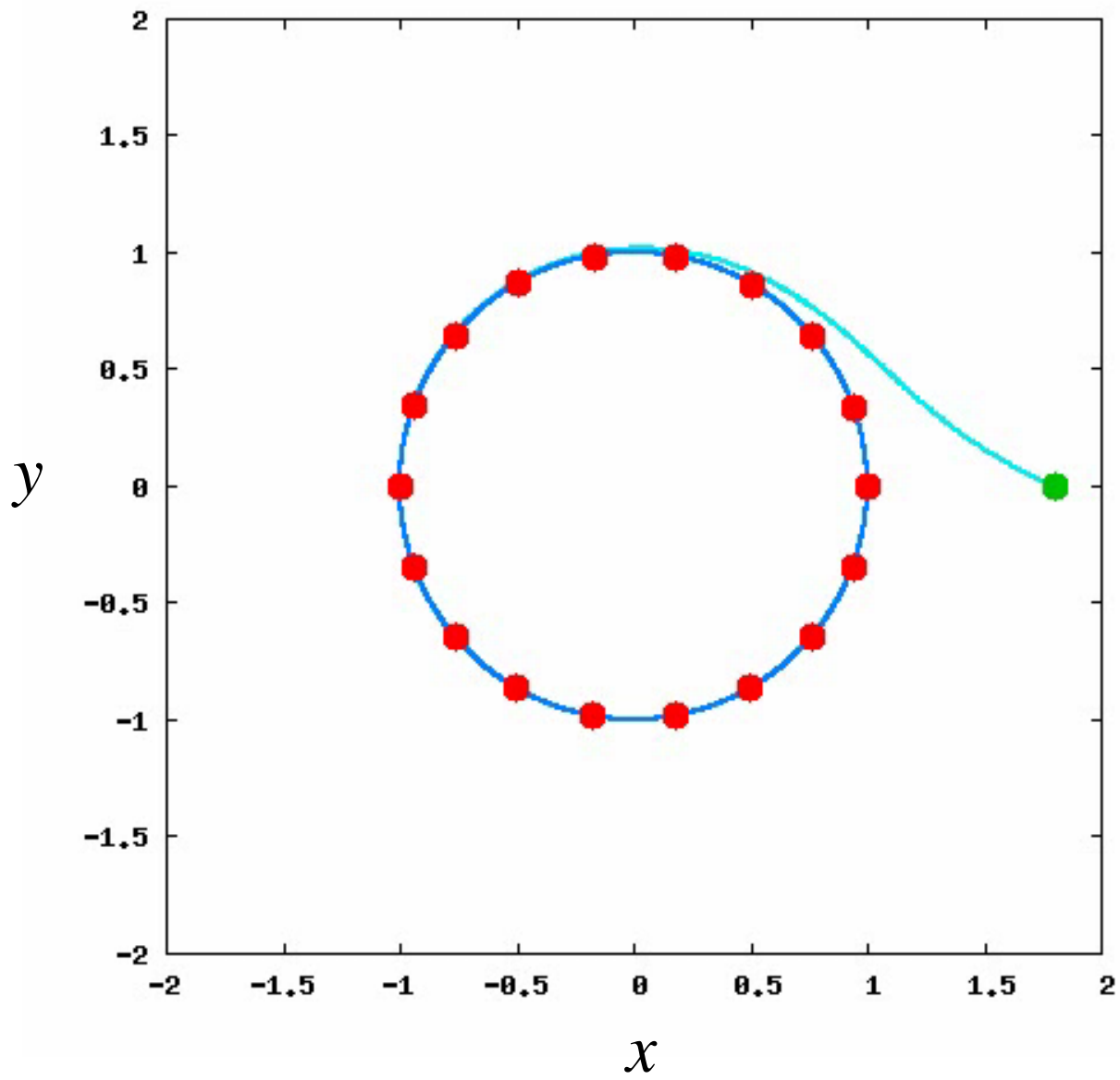


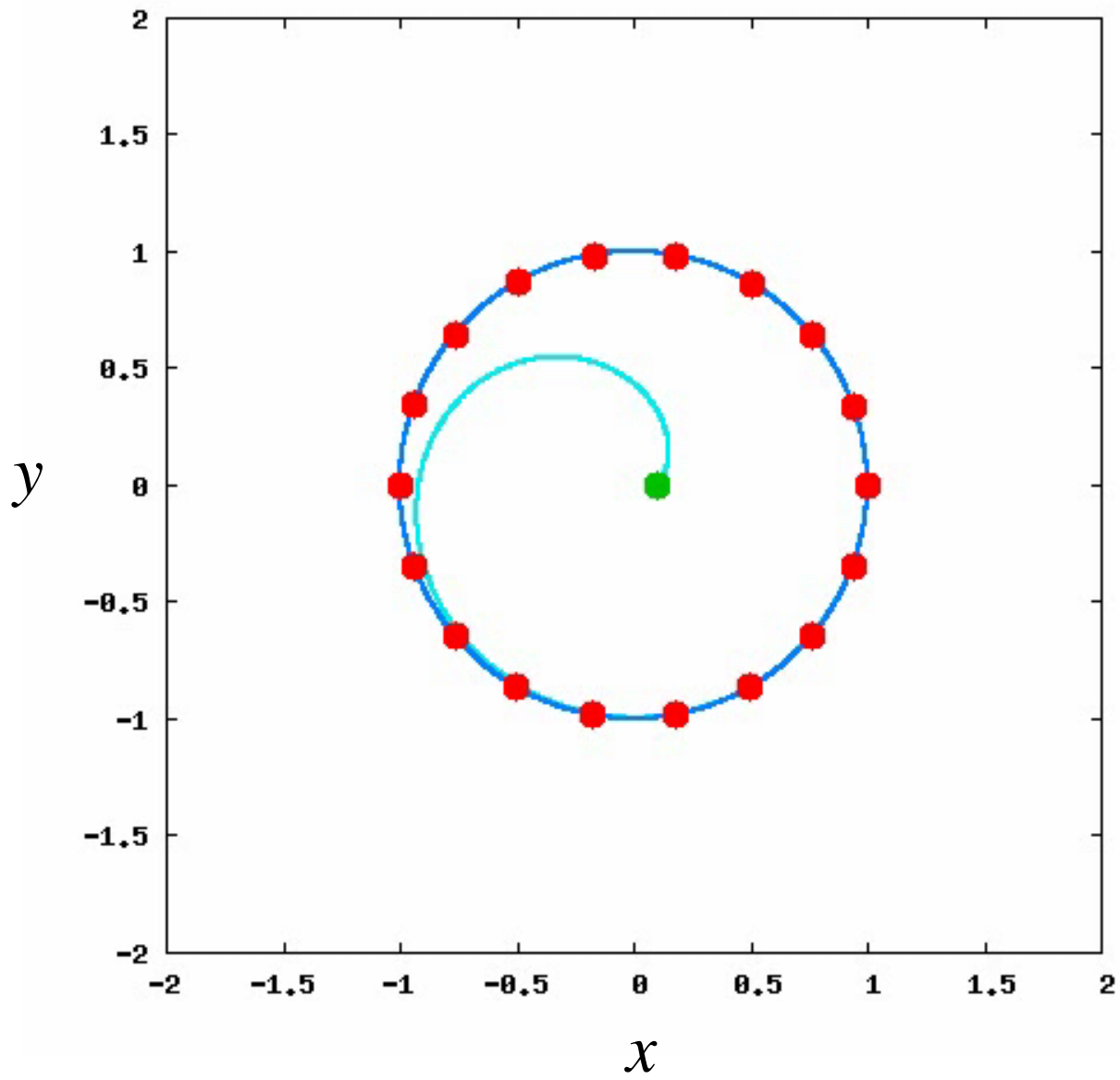
x

Limit Cycle (極限軌道)

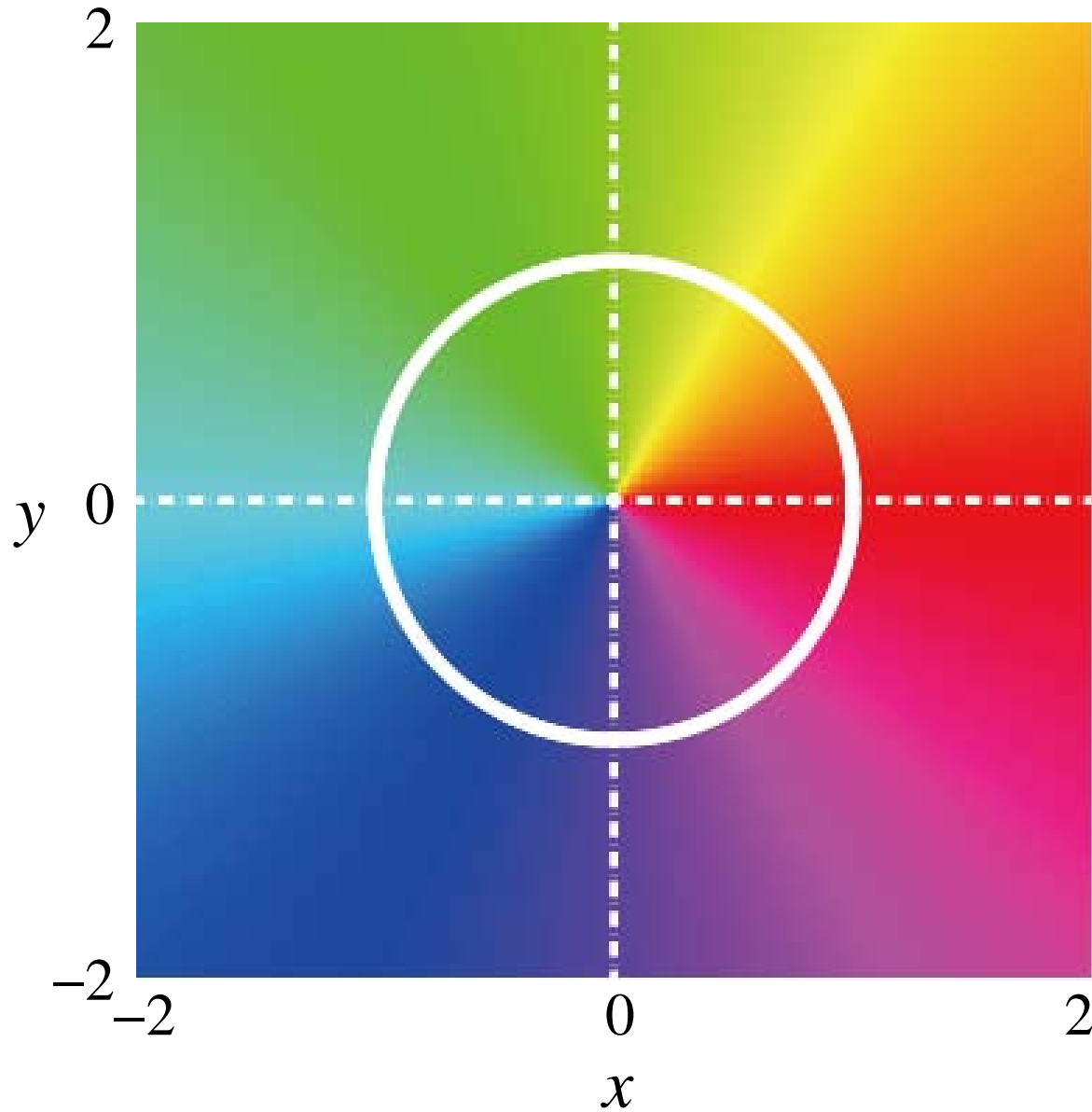
リミットサイクル上の運動







等位相面

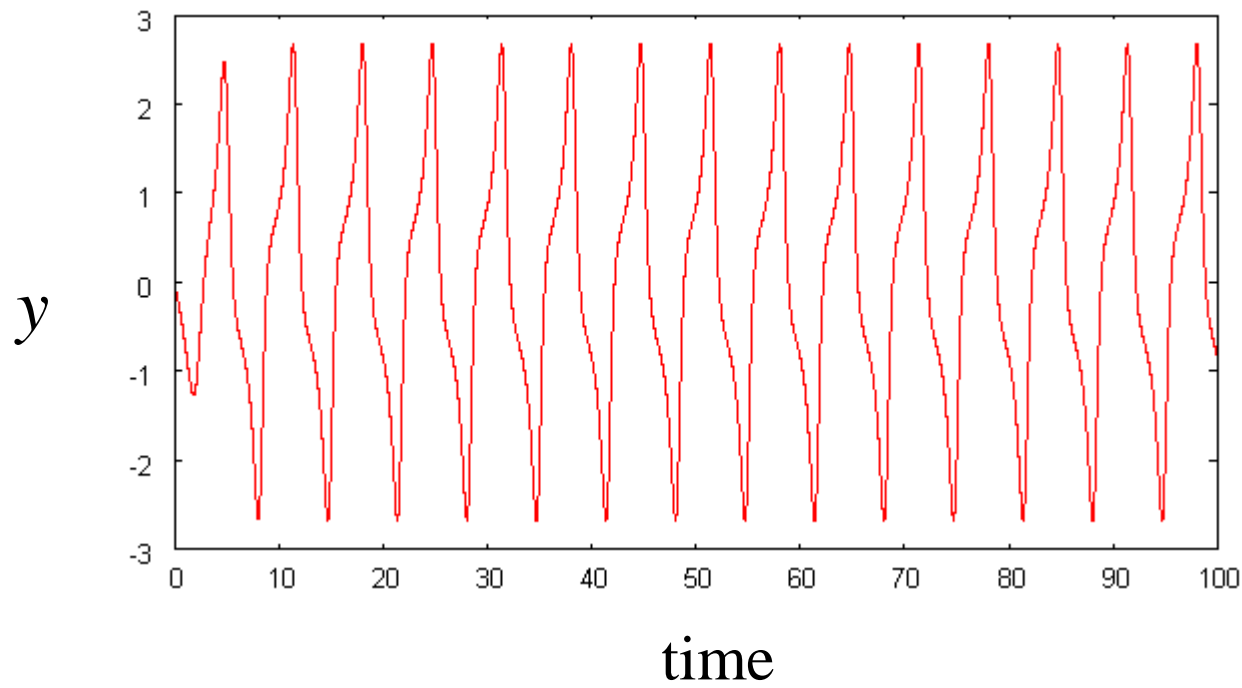
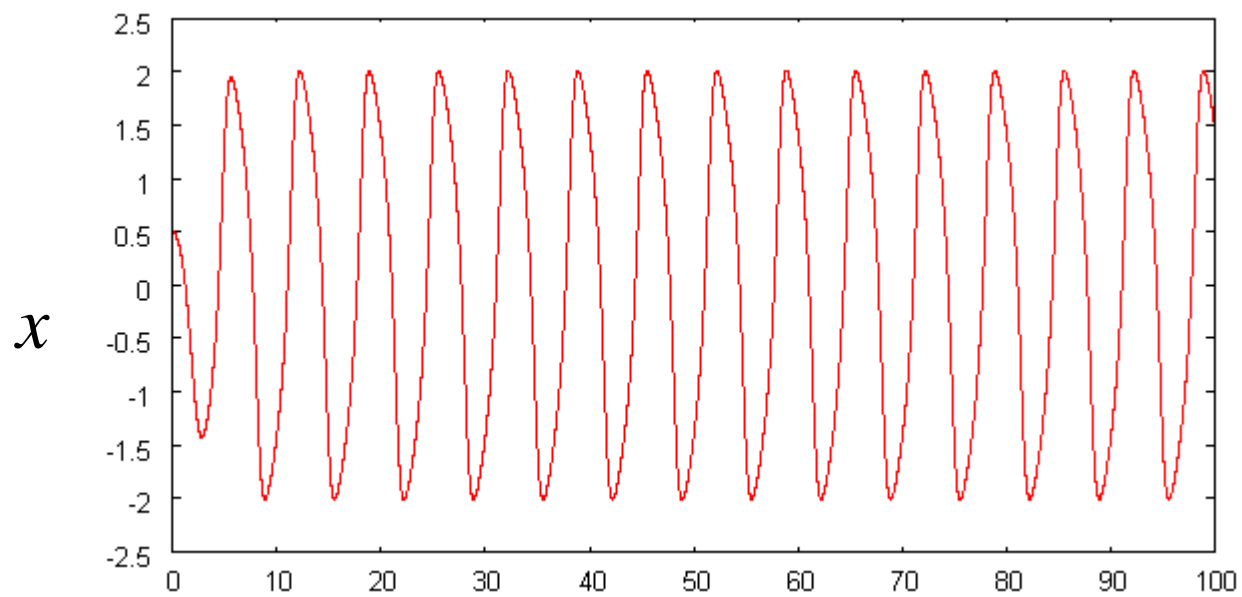


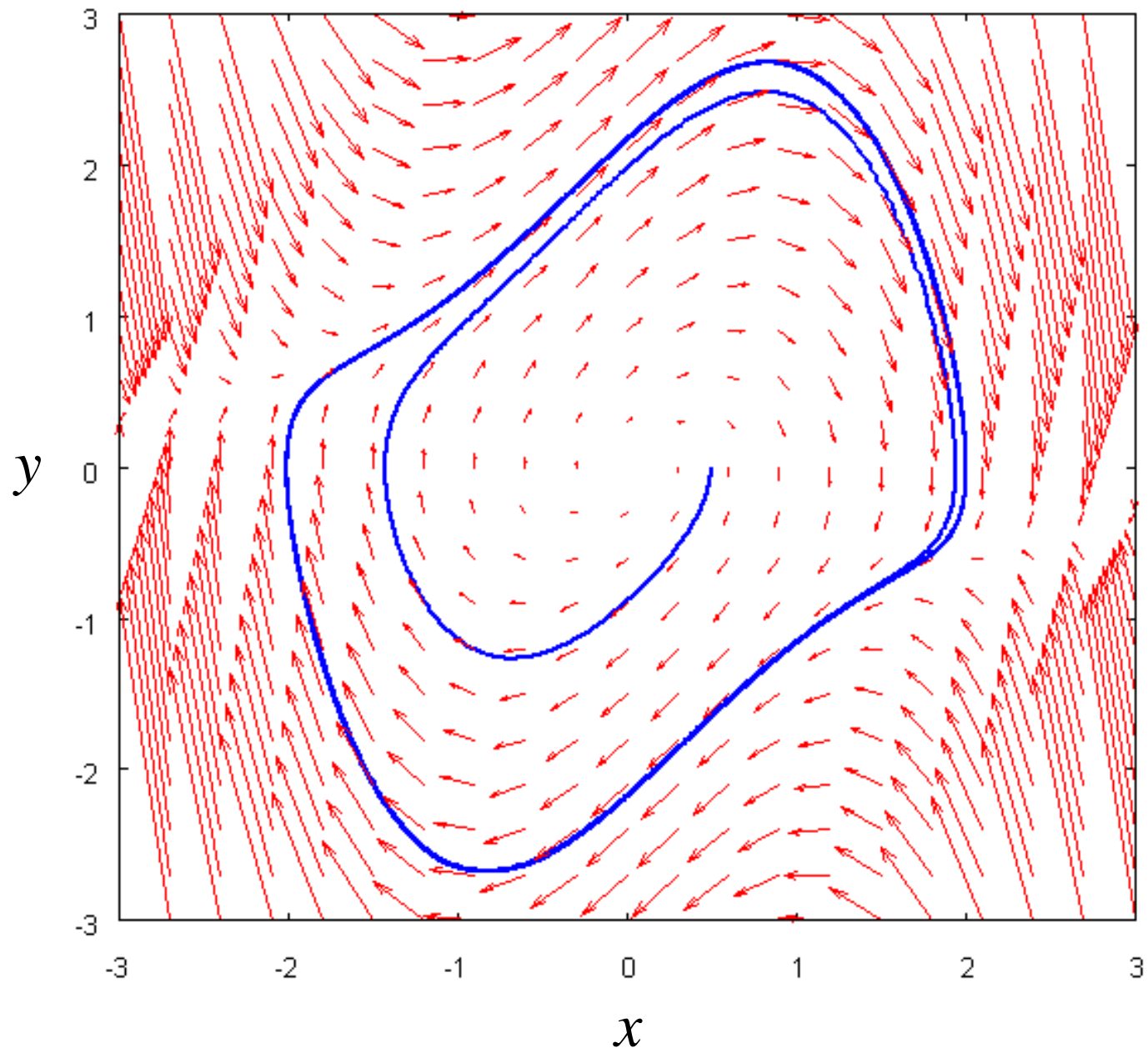
$$\theta = \arctan\left(\frac{y}{x}\right)$$

van del Pol 方程式 ~ 丸くなくても...

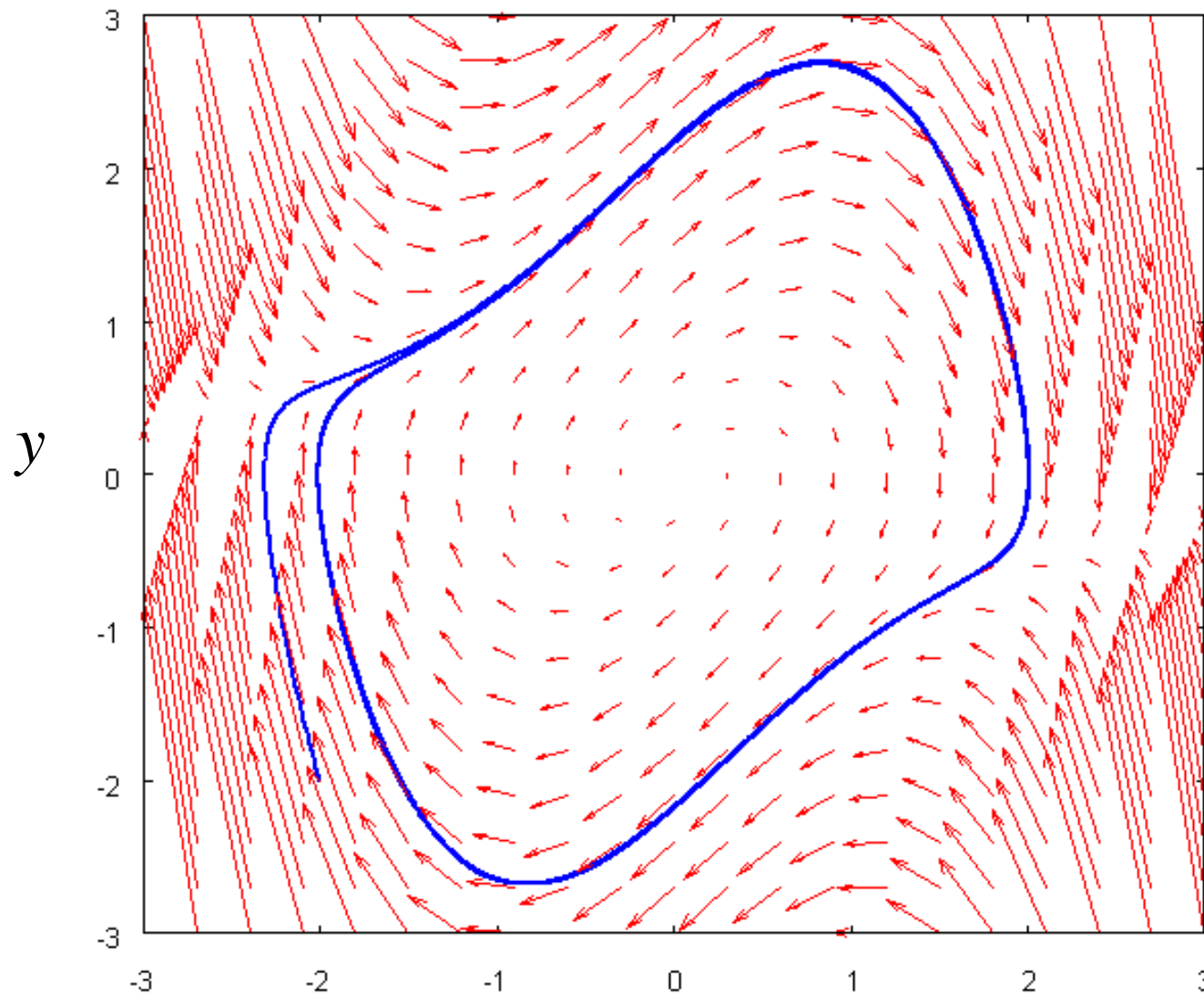
$$\frac{d^2 x}{dt^2} + \alpha(x^2 - 1)\frac{dx}{dt} + x = 0$$

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





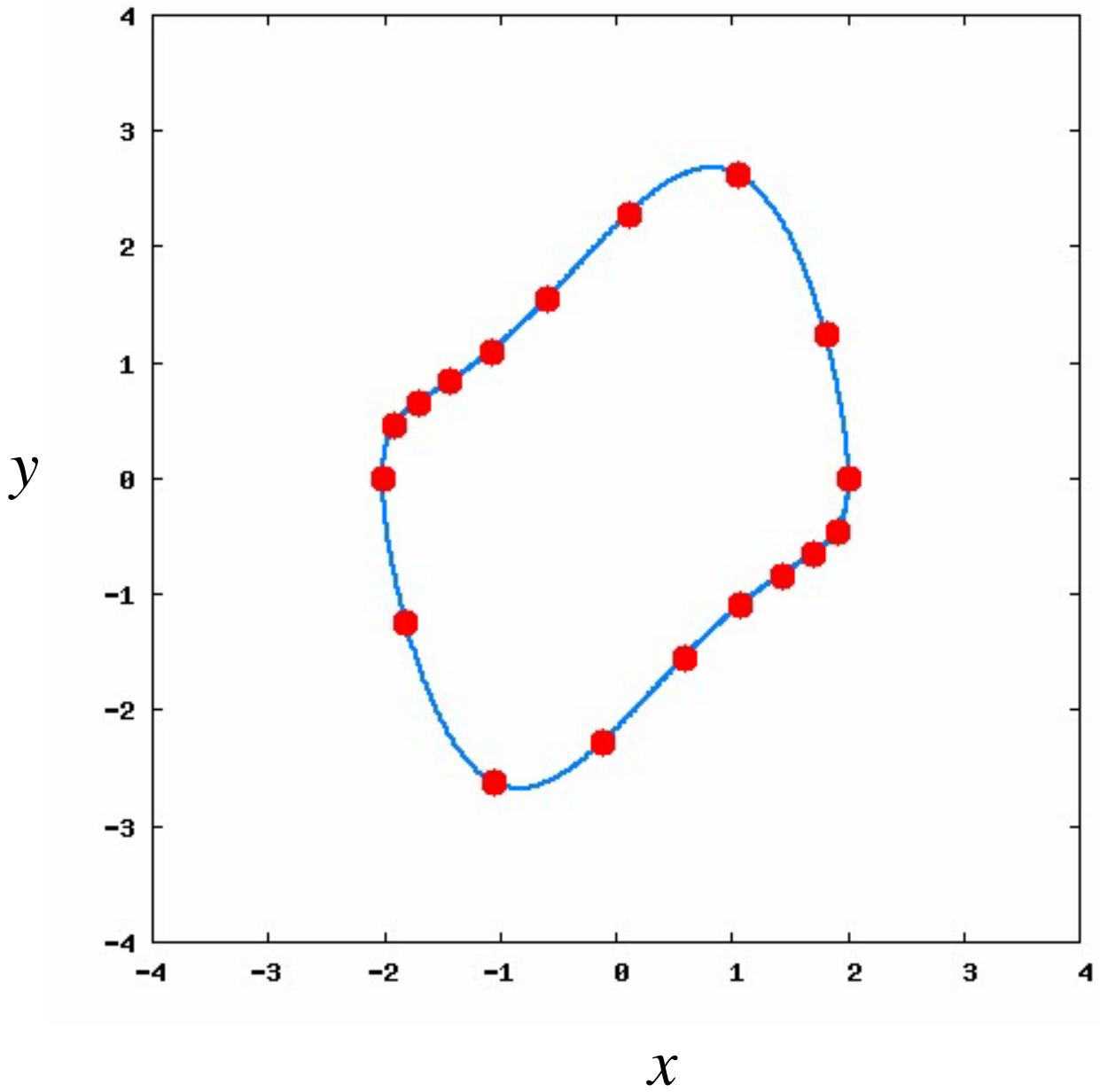
初期値を変えても

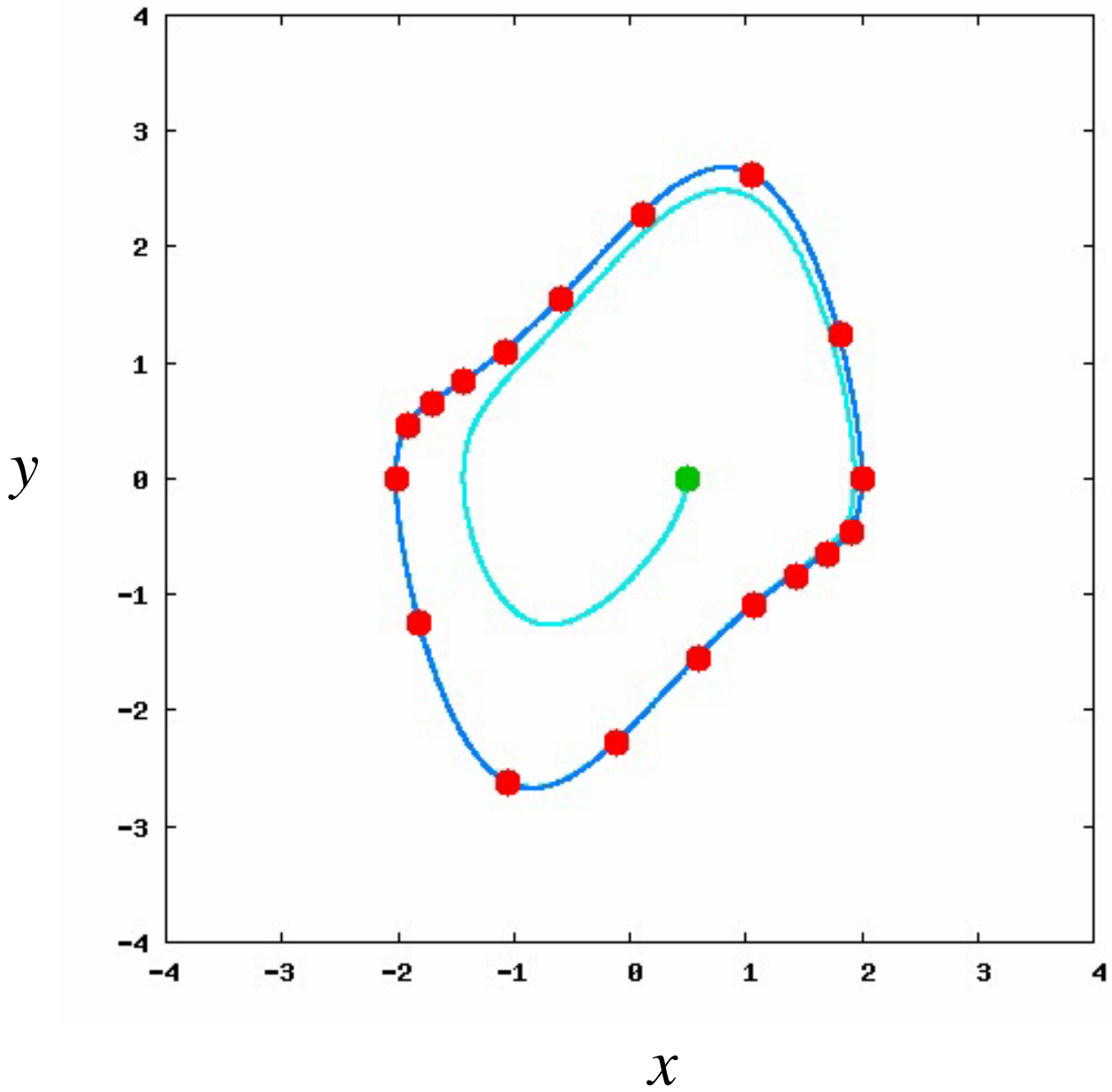


Limit Cycle (極限軌道)

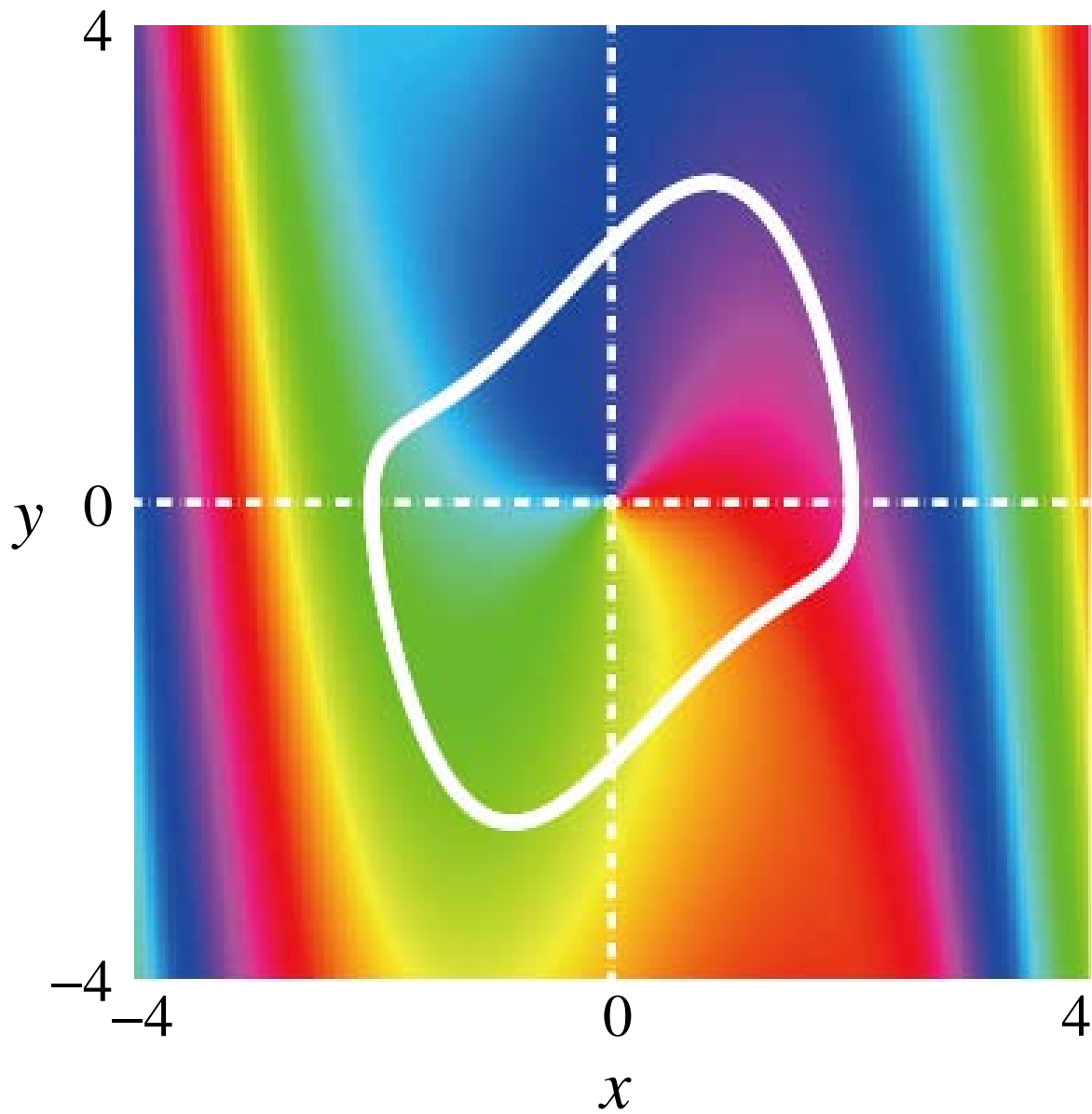
x

y





等位相面



さまざまな非線形振動子

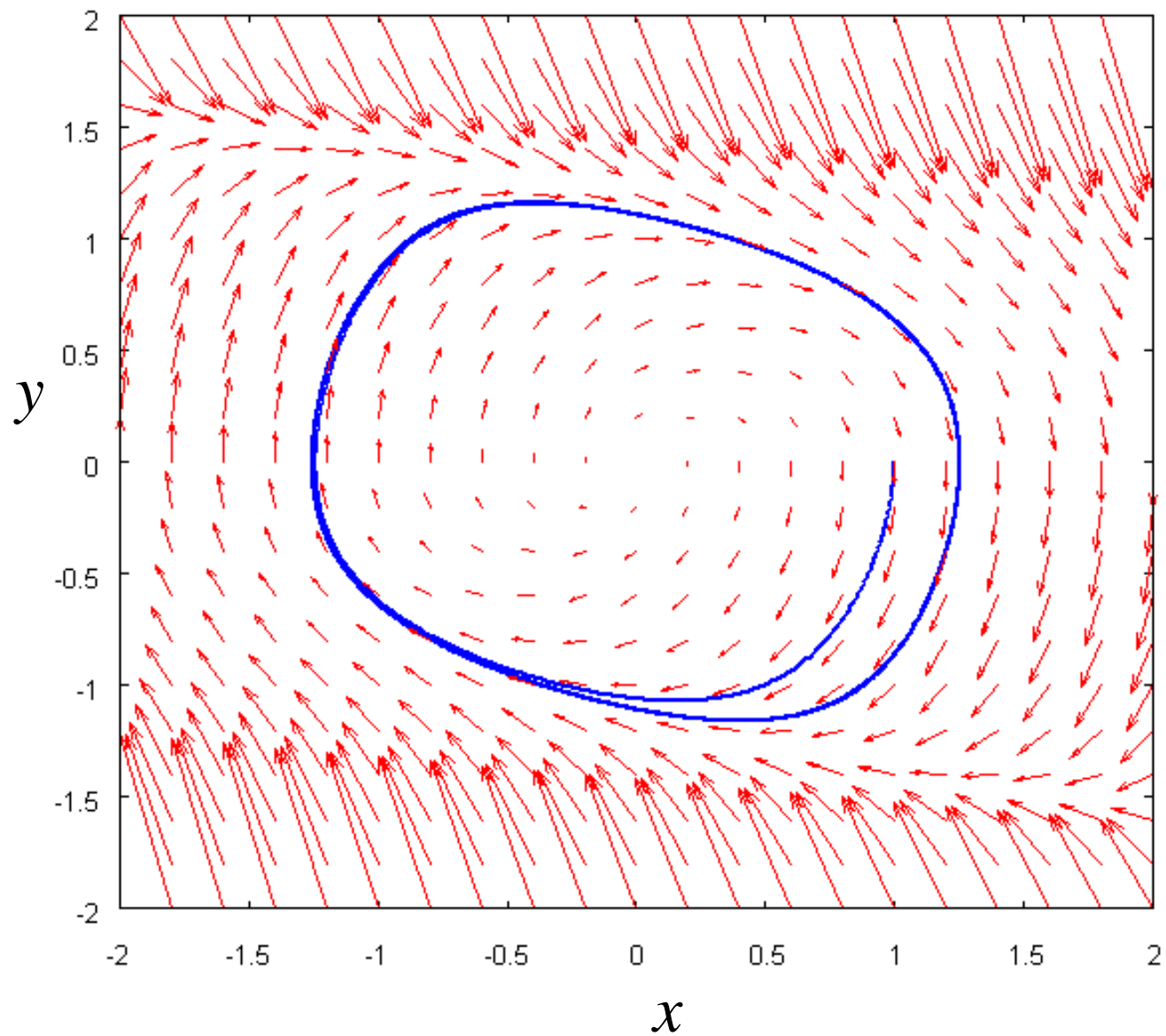
Rayleigh方程式

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

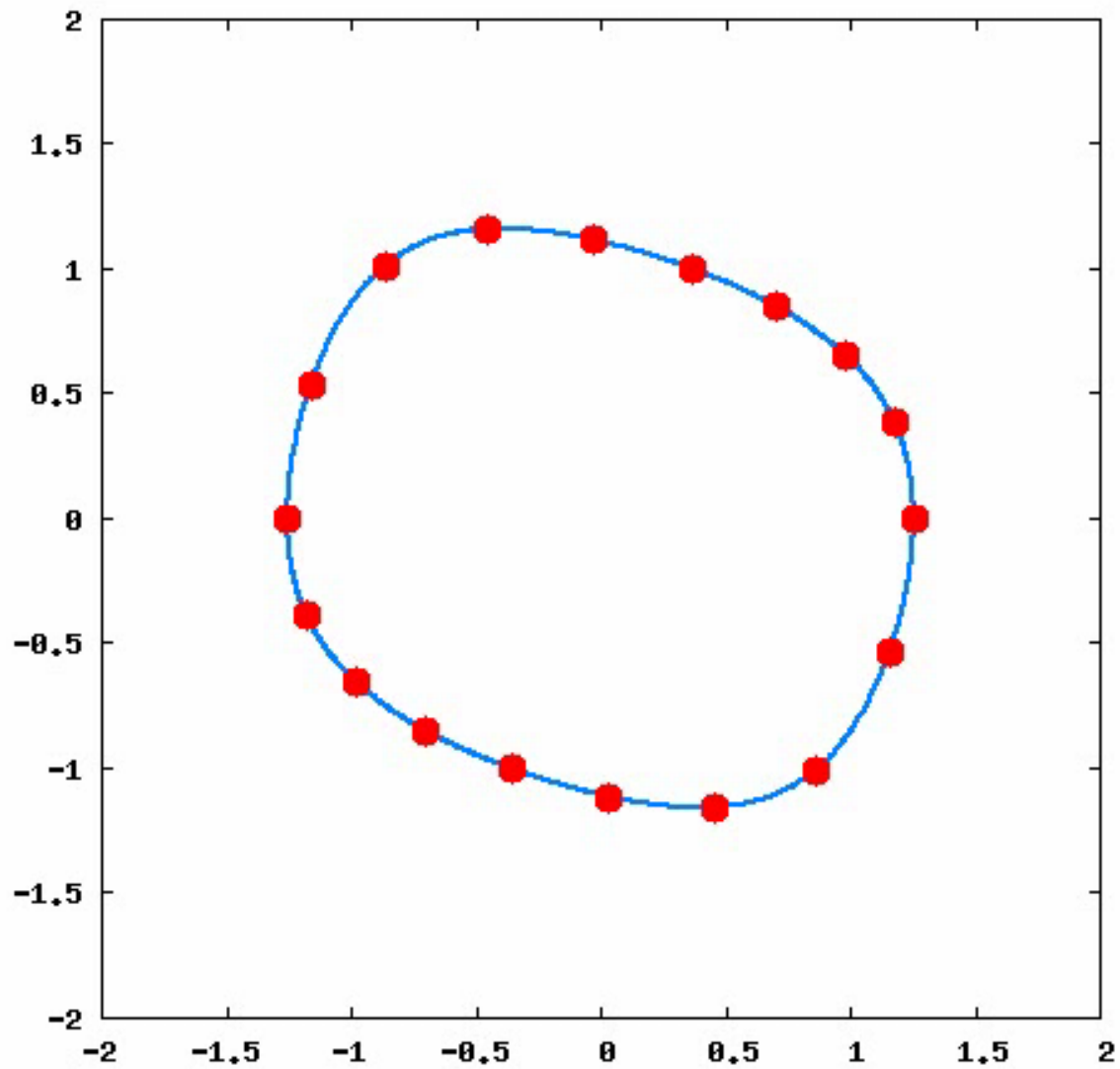
FitzHugh-Nagumo方程式

$$\begin{cases} \frac{dx}{dt} = \frac{1}{\varepsilon} (x - x^3 - y) \\ \frac{dy}{dt} = x - y + b \end{cases}$$

Rayleigh方程式

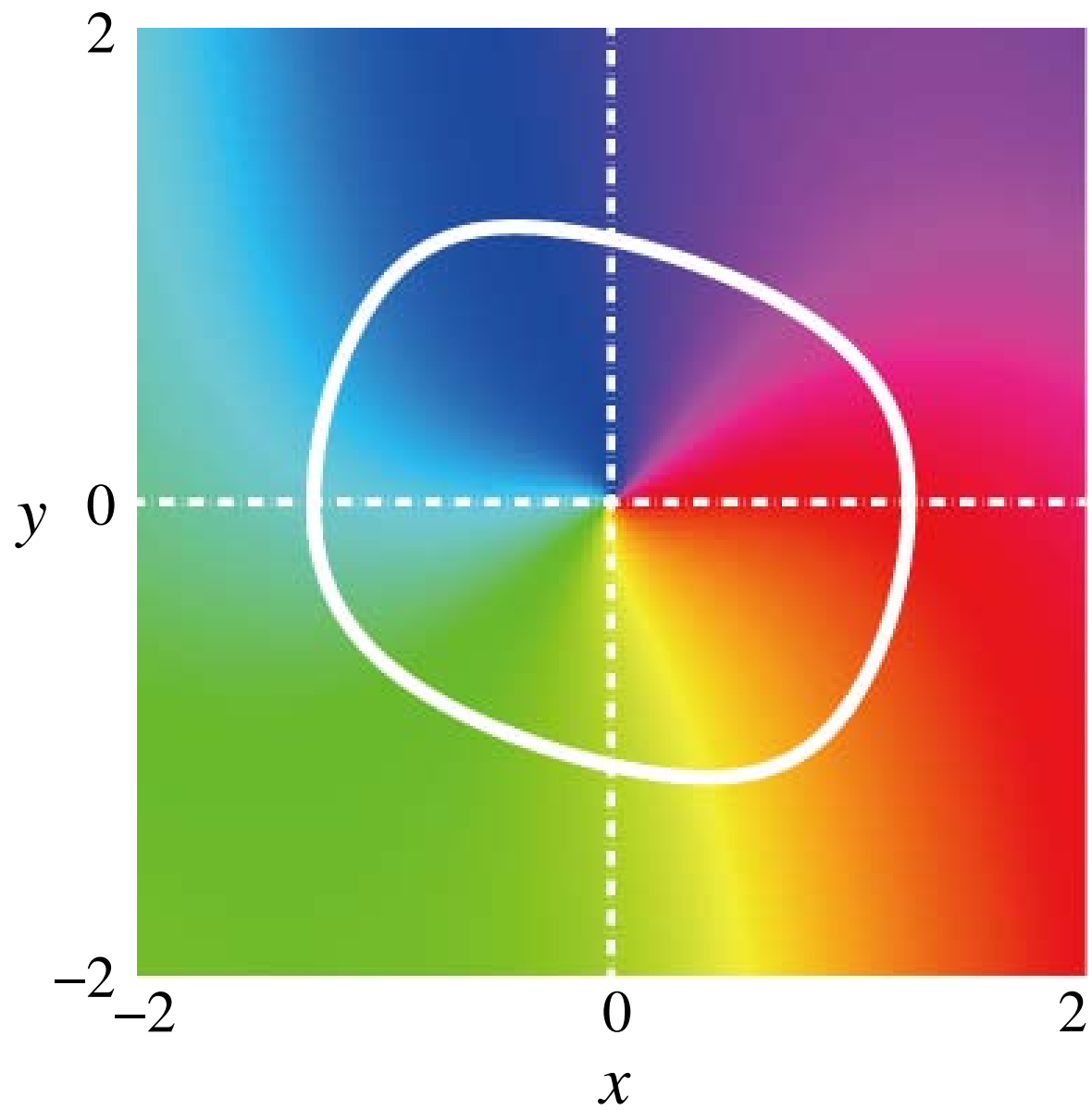


y

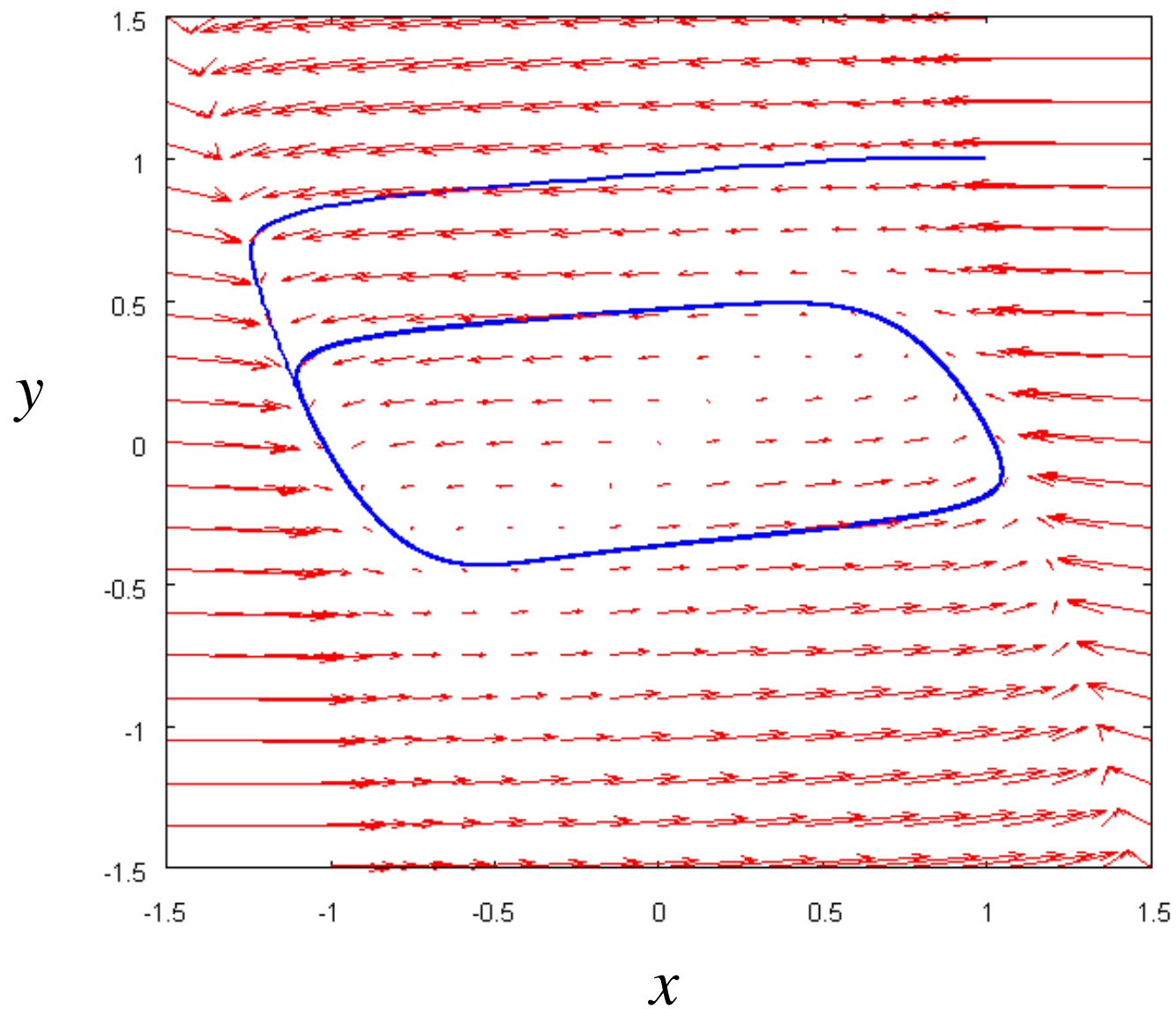


x

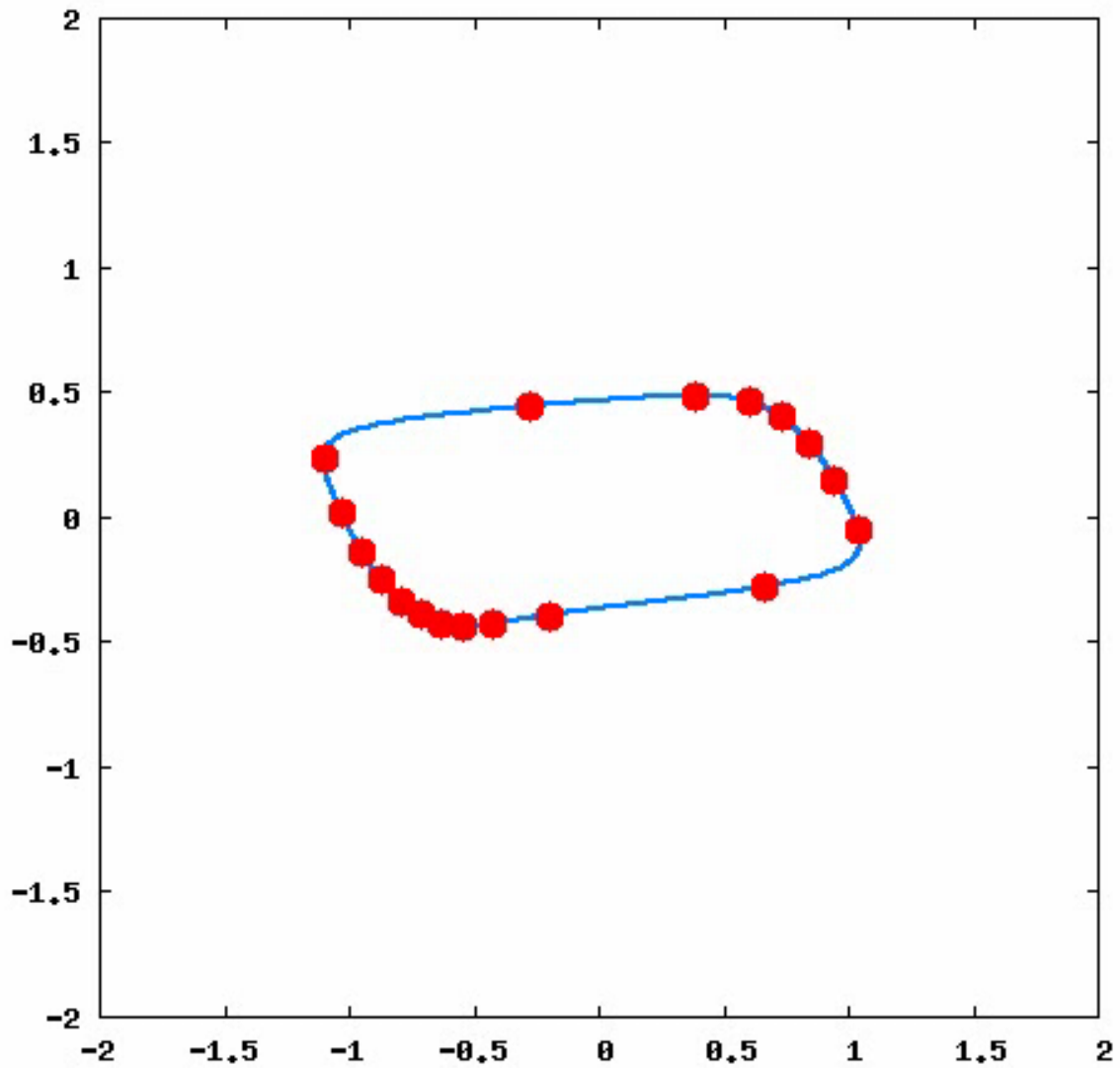
等位相面



FitzHugh-Nagumo方程式

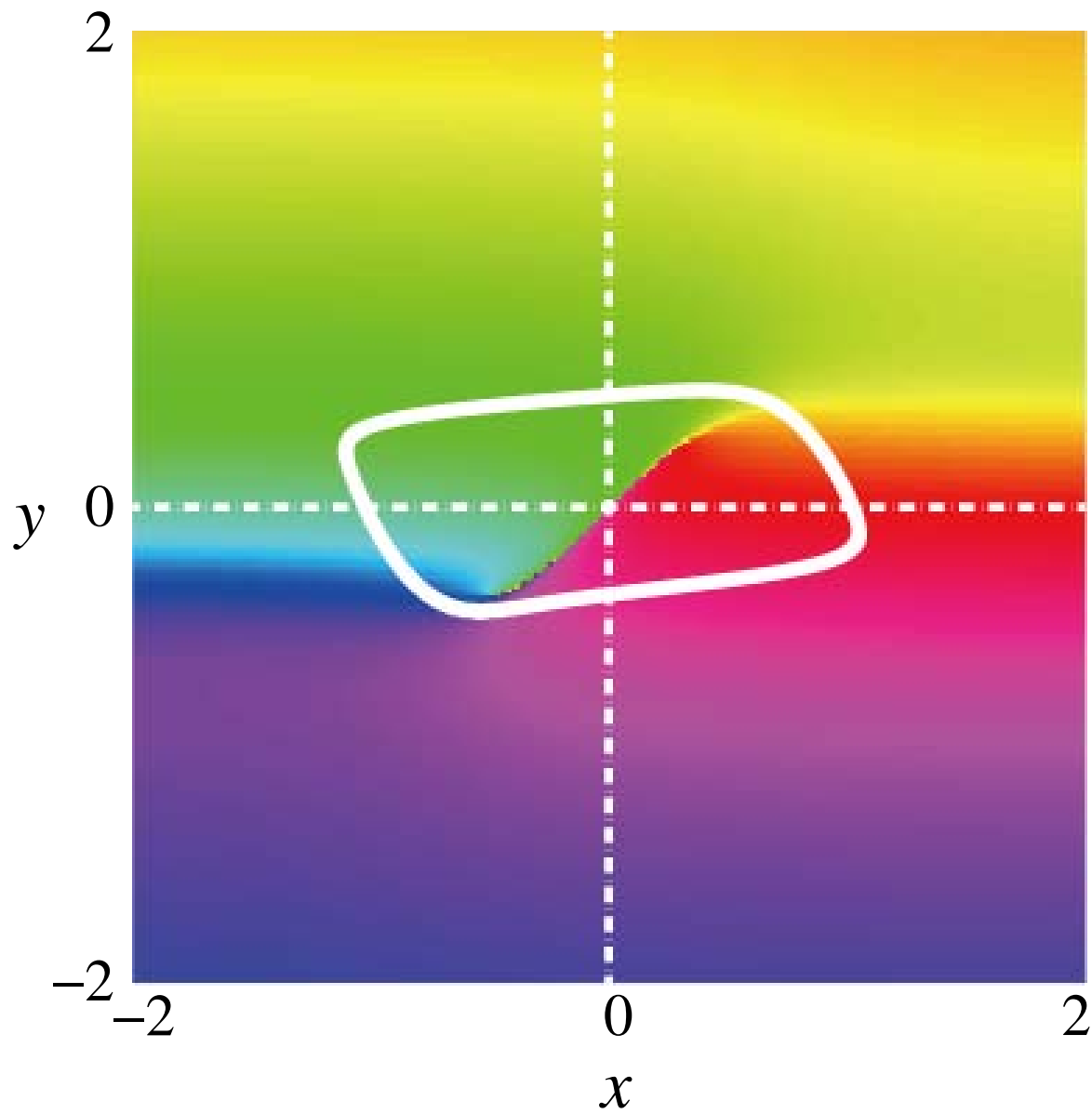


y



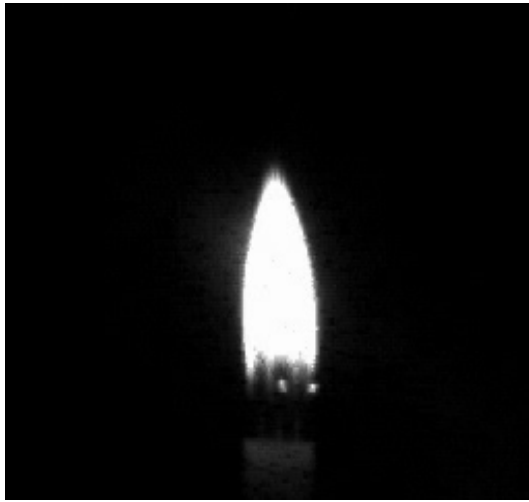
x

等位相面



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



candle oscillator



BR reaction



saline oscillator



Plastic-bottle oscillator



water-camphor system

Belousov-Zhabotinsky (BZ)反応の実験

攪拌した系で

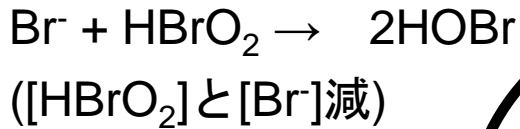


1 cm

空間勾配はなし

BZ反応のメカニズム

Step I. $[\text{Br}^-]$ 高の時

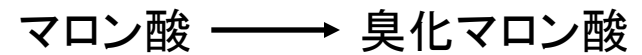


抑制因子(Br^-)

Step III.

金属触媒の還元

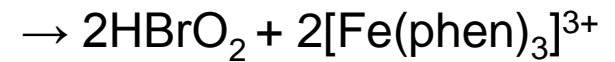
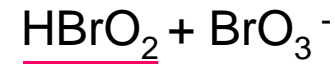
(臭化マロン酸とマロン酸による)



Step II. $[\text{Br}^-]$ 低の時

金属触媒の酸化

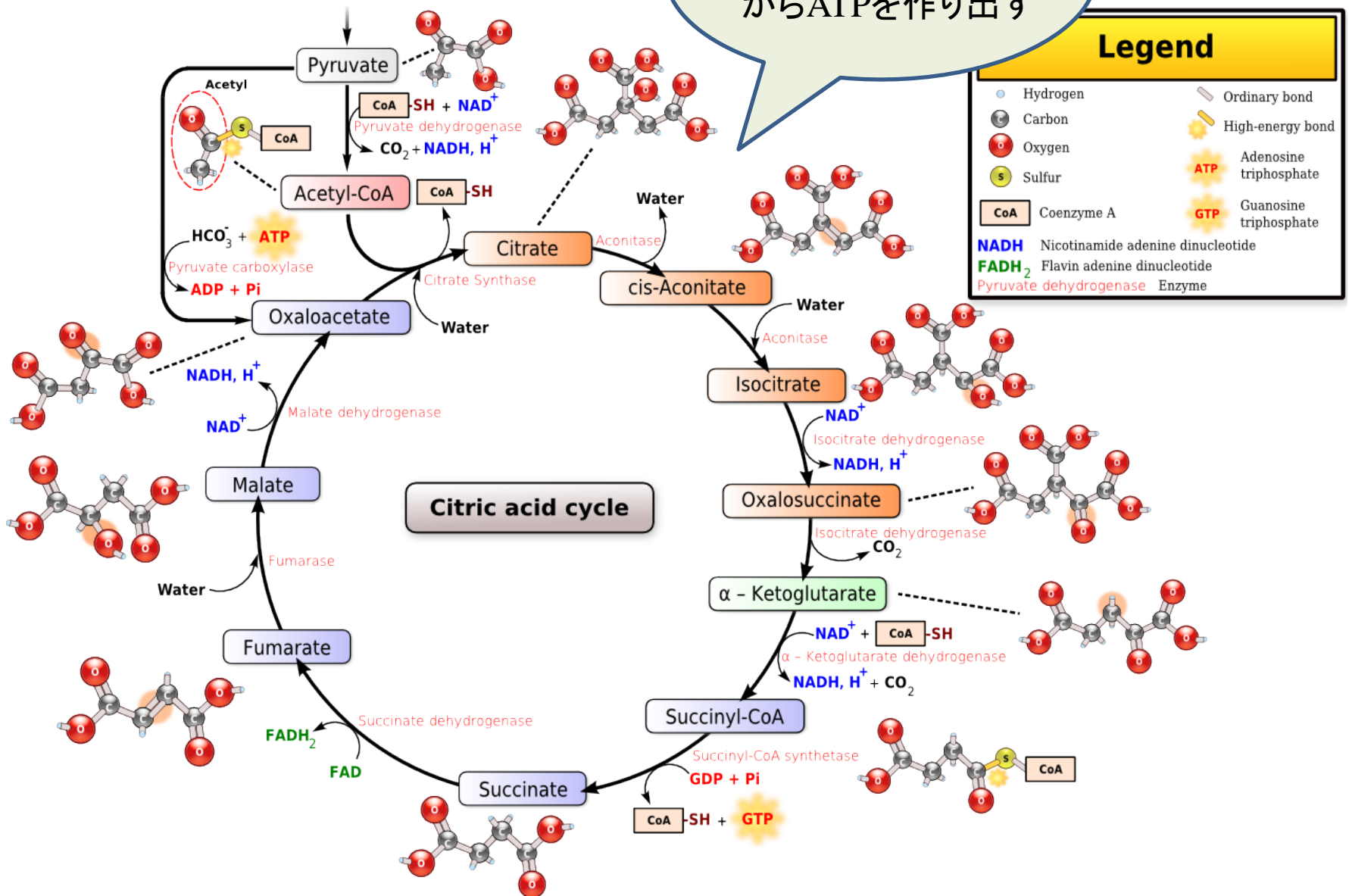
活性因子(HBrO_2)を自己触媒的に生成



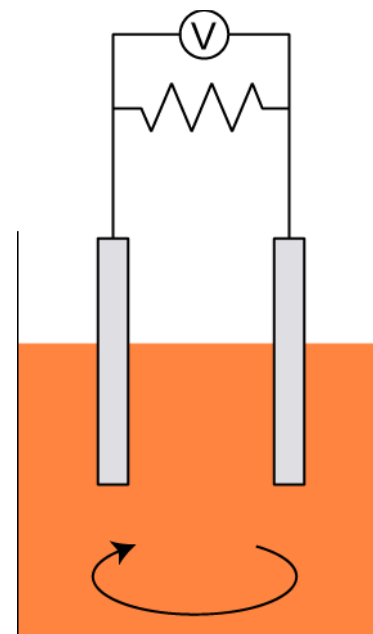
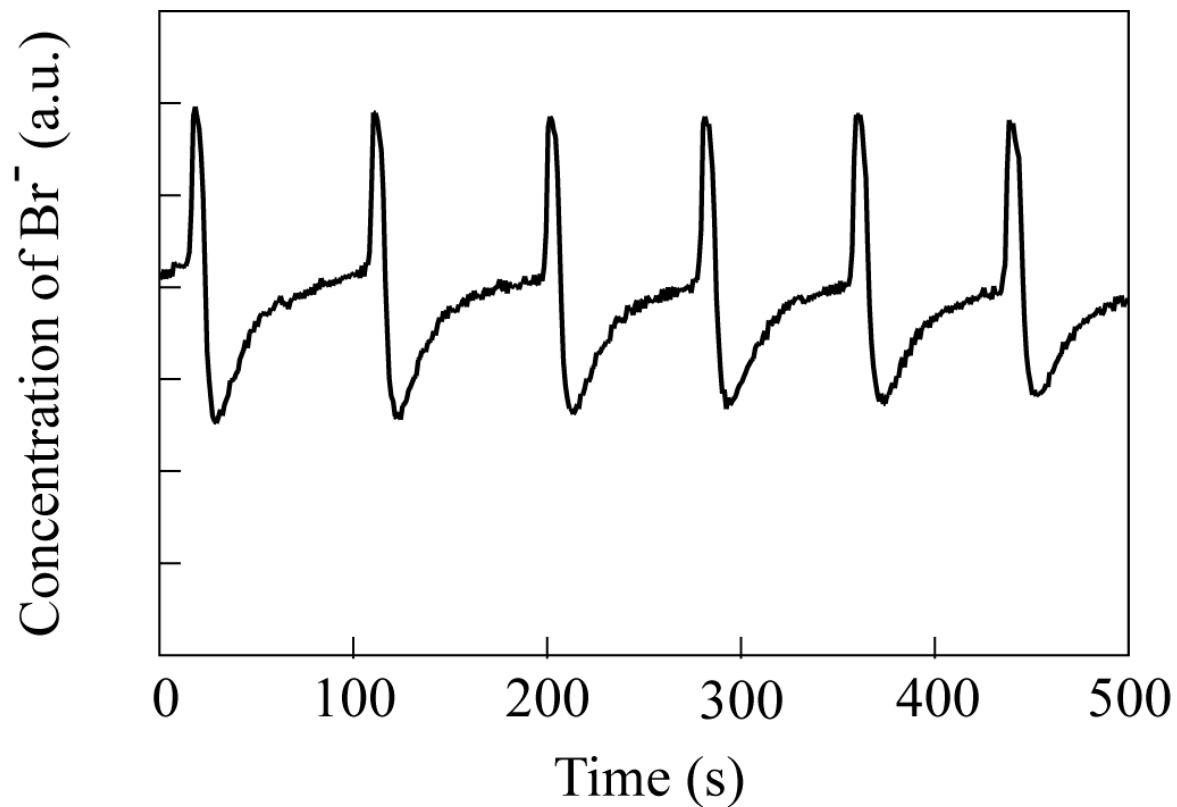
酸化反応 と 還元反応 が交互に起こる

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



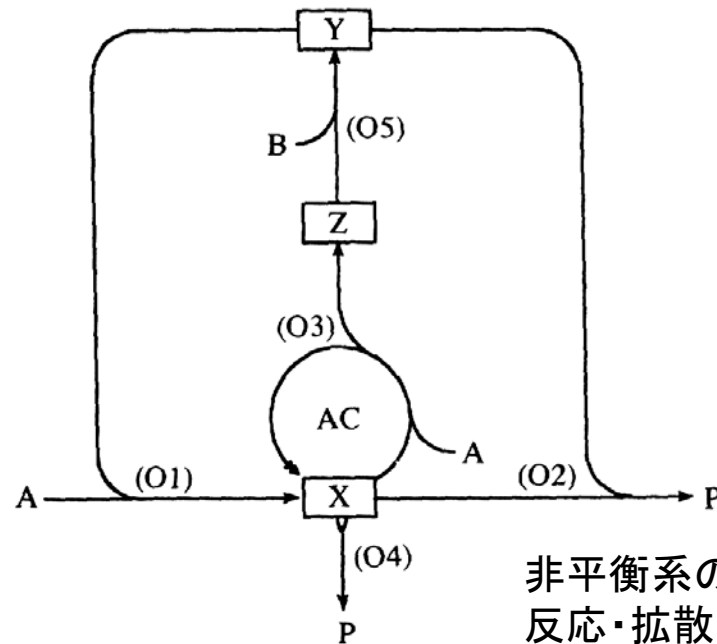
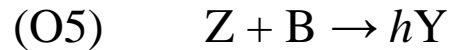
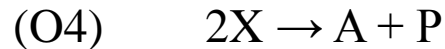
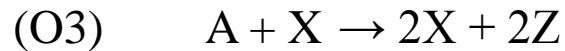
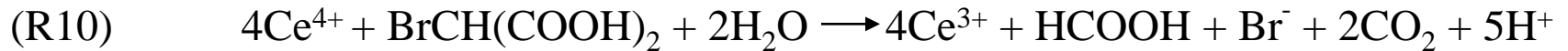
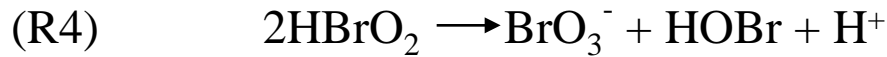
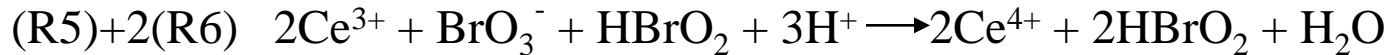
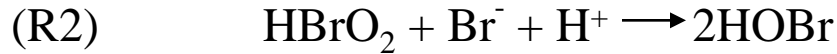
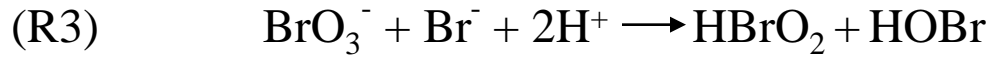
BZ反応のモデル化

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).

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

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

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

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

U : [HBrO₂]

V : [Fe(phen)₃³⁺]



青色

2変数Oregonator

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

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

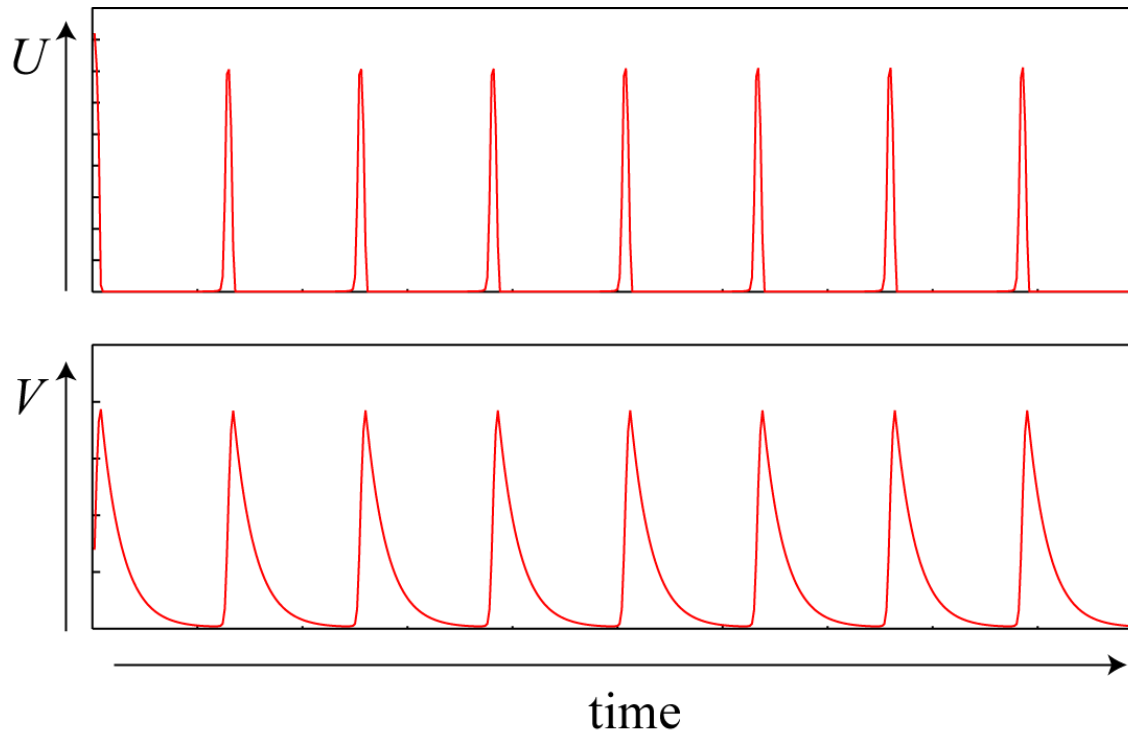
U : [HBrO₂]

V : [Fe(phen)₃³⁺]

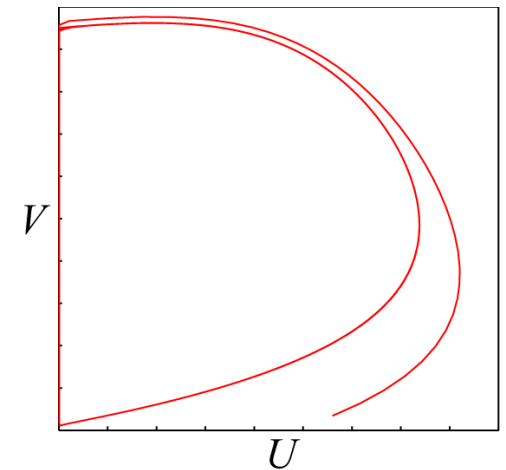
青色

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

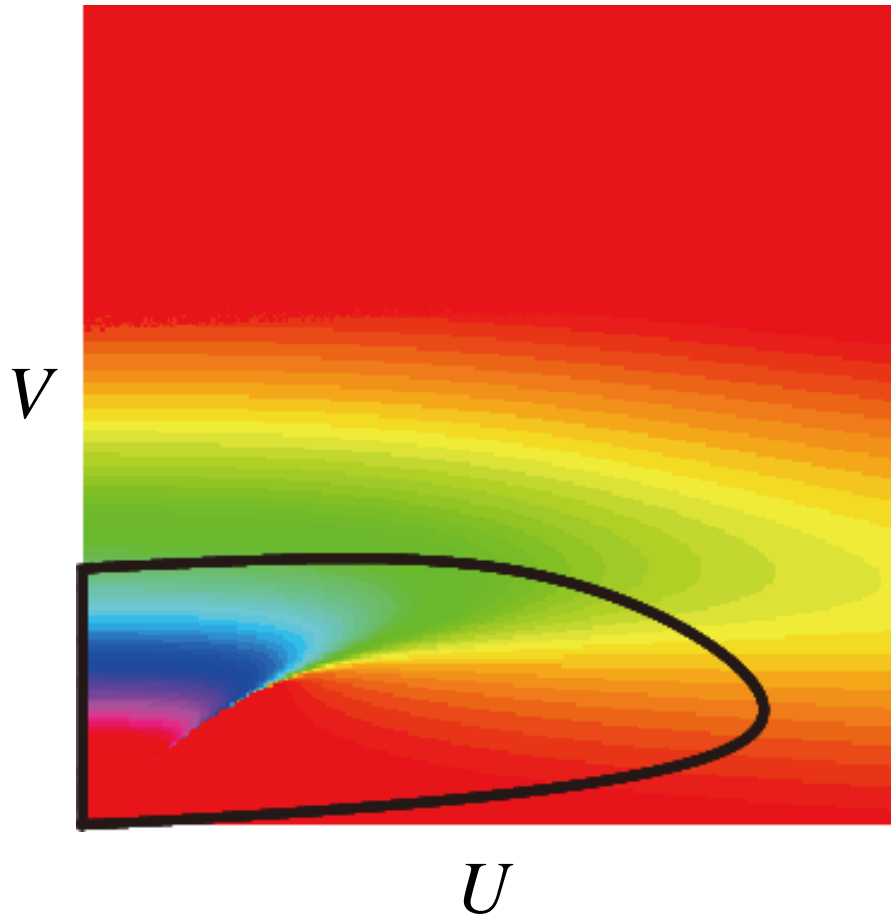
数値計算:



相平面で見ると

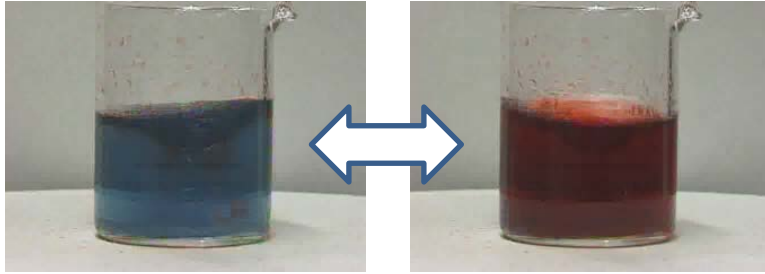


Oregonatorの等位相面



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

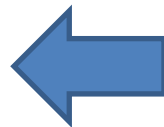
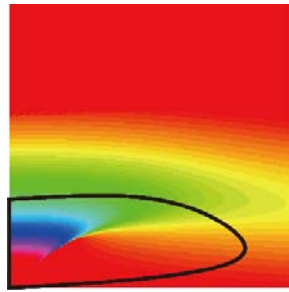
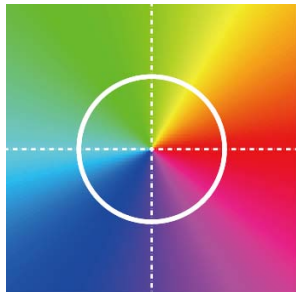
化学反応式 (物質に近いモデル)

- (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) $\text{BrO}_2 \cdot + \text{Ce}^{3+} + \text{H}^+ \rightleftharpoons \text{HBrO}_2 + \text{Ce}^{4+}$
- (R7) $\text{BrO}_2 \cdot + \text{Ce}^{4+} + \text{H}_2\text{O} \rightleftharpoons \text{BrO}_3^- + \text{Ce}^{3+} + 2\text{H}^+$
- (R8) $\text{Br}_2 + \text{CH}_2(\text{COOH})_2 \rightarrow \text{BrCH}(\text{COOH})_2 + \text{Br}^- + \text{H}^+$
- (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 : $[\text{HBrO}_2]$

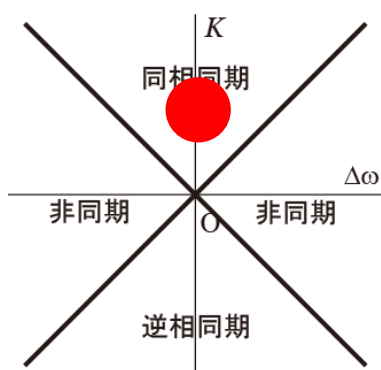
V : $[\text{Fe}(\text{phen})_3^{3+}]$

青色

非線形振動子の結合系

2振動子の結合系

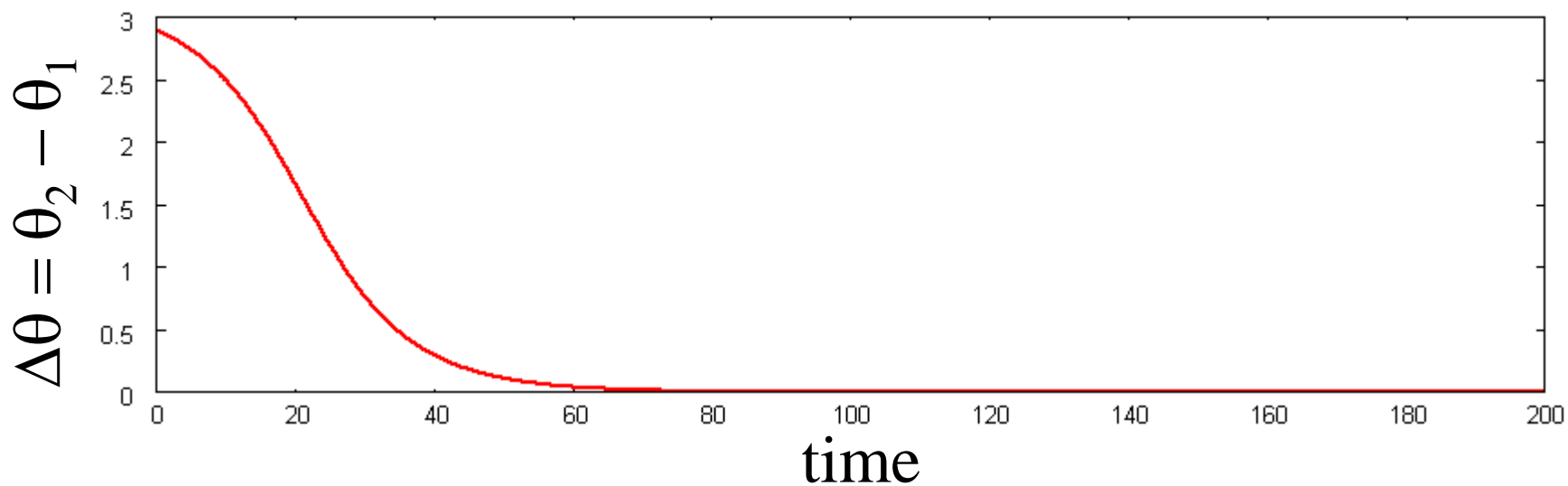
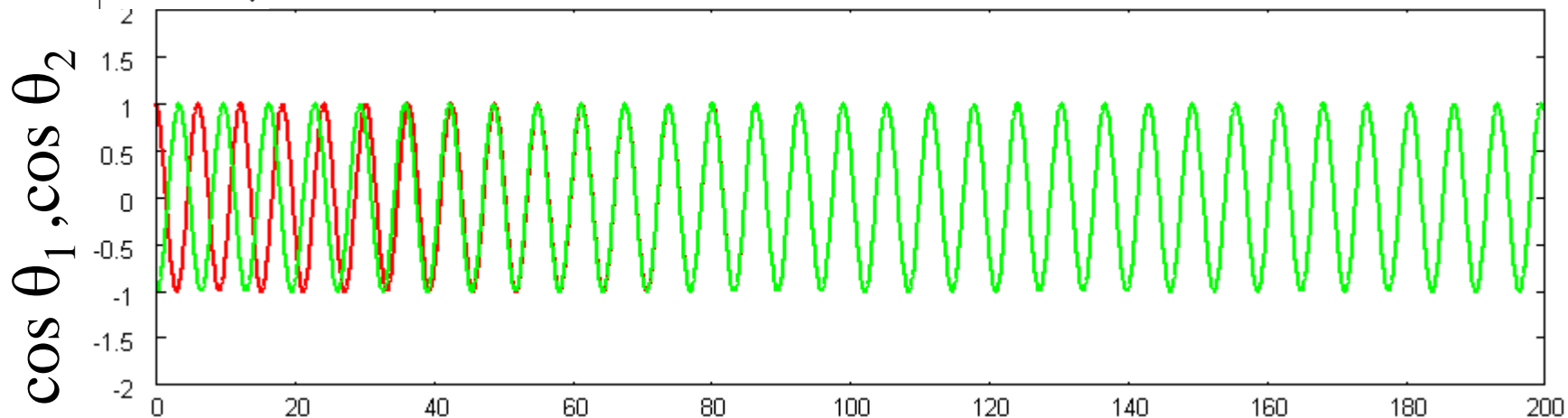
$$\left\{ \begin{array}{l} \frac{d\theta_1}{dt} = \omega_1 + K \sin(\theta_2 - \theta_1) \\ \frac{d\theta_2}{dt} = \omega_2 + K \sin(\theta_1 - \theta_2) \end{array} \right.$$

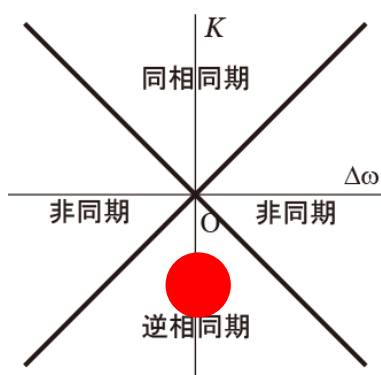


$$\begin{cases} \frac{d\theta_1}{dt} = \omega_1 + K \sin(\theta_2 - \theta_1) \\ \frac{d\theta_2}{dt} = \omega_2 + K \sin(\theta_1 - \theta_2) \end{cases}$$

$$\omega_1 = \omega_2 = 1$$

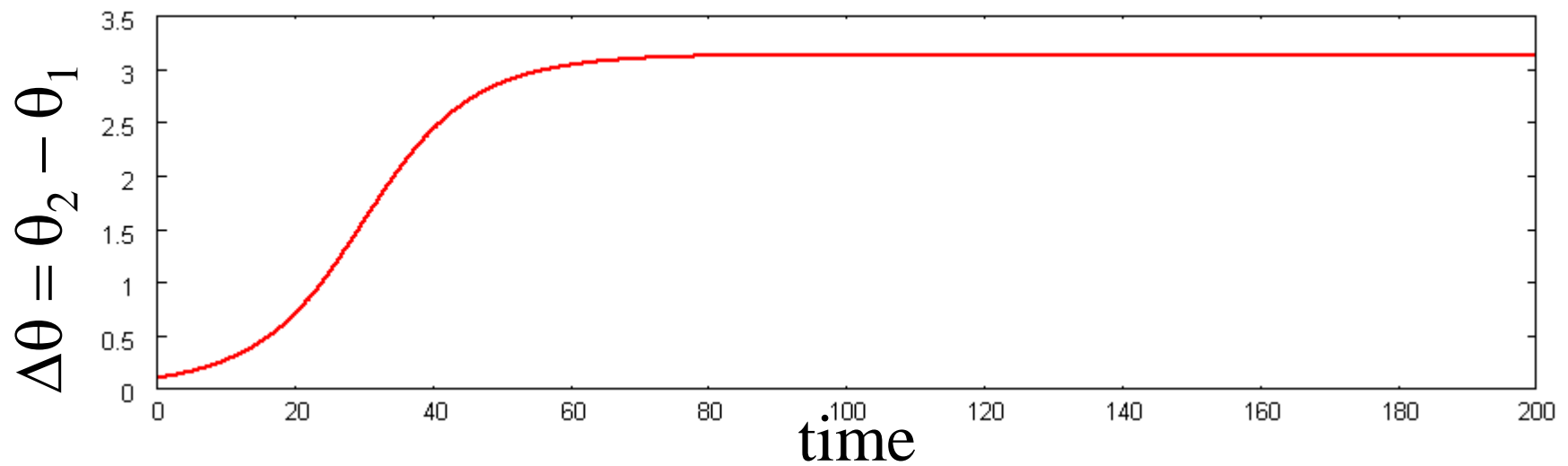
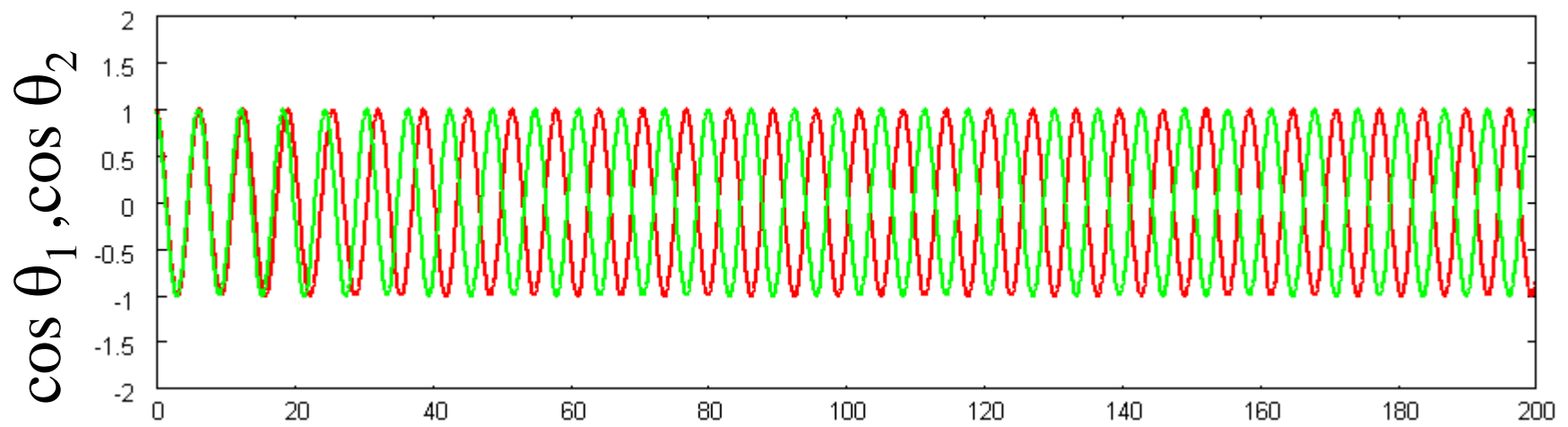
$$K = 0.05$$

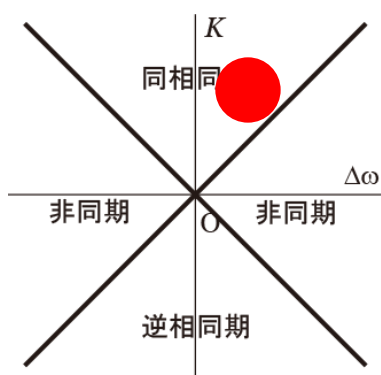




$$\begin{cases} \frac{d\theta_1}{dt} = \omega_1 + K \sin(\theta_2 - \theta_1) \\ \frac{d\theta_2}{dt} = \omega_2 + K \sin(\theta_1 - \theta_2) \end{cases}$$

$$\begin{aligned} \omega_1 &= \omega_2 = 1 \\ K &= -0.05 \end{aligned}$$

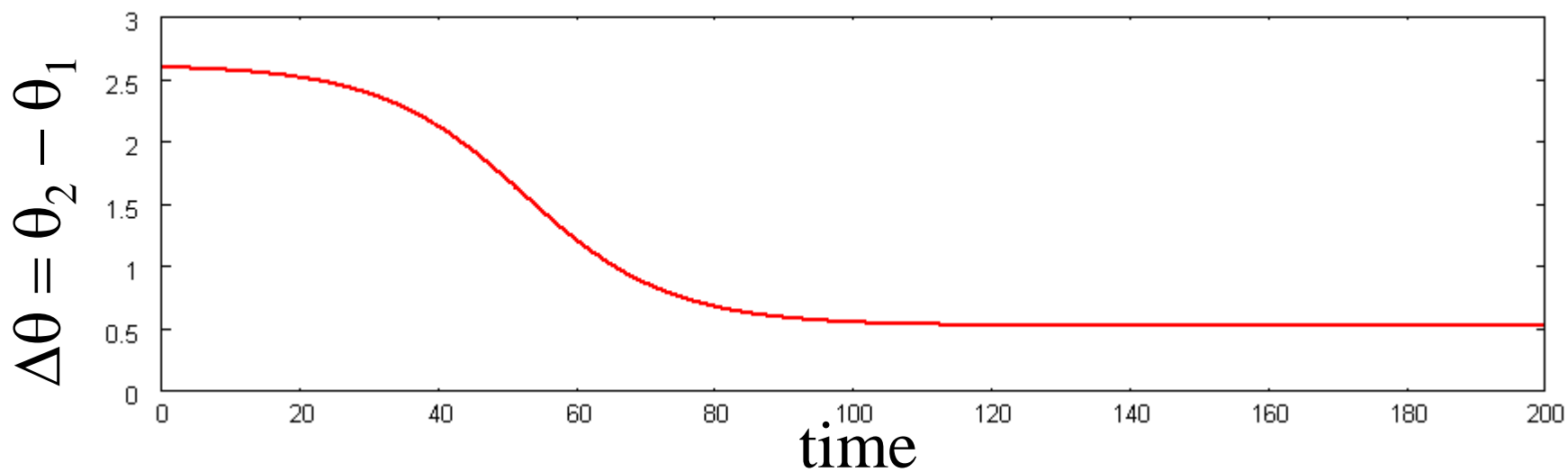
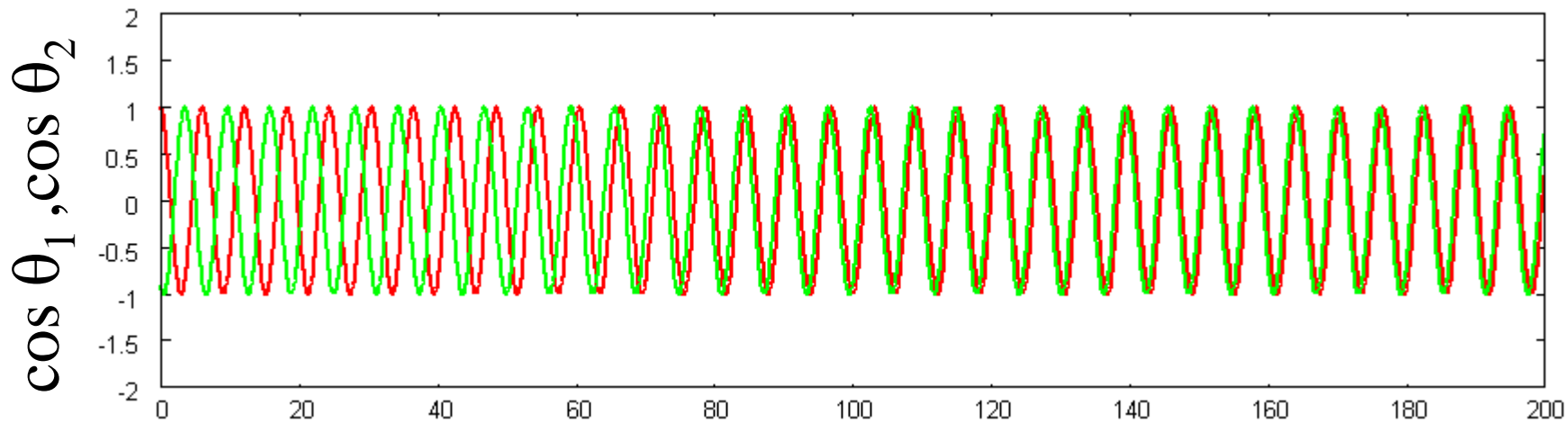


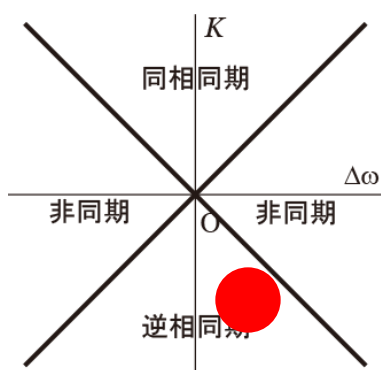


$$\begin{cases} \frac{d\theta_1}{dt} = \omega_1 + K \sin(\theta_2 - \theta_1) \\ \frac{d\theta_2}{dt} = \omega_2 + K \sin(\theta_1 - \theta_2) \end{cases}$$

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

$$K = 0.05$$

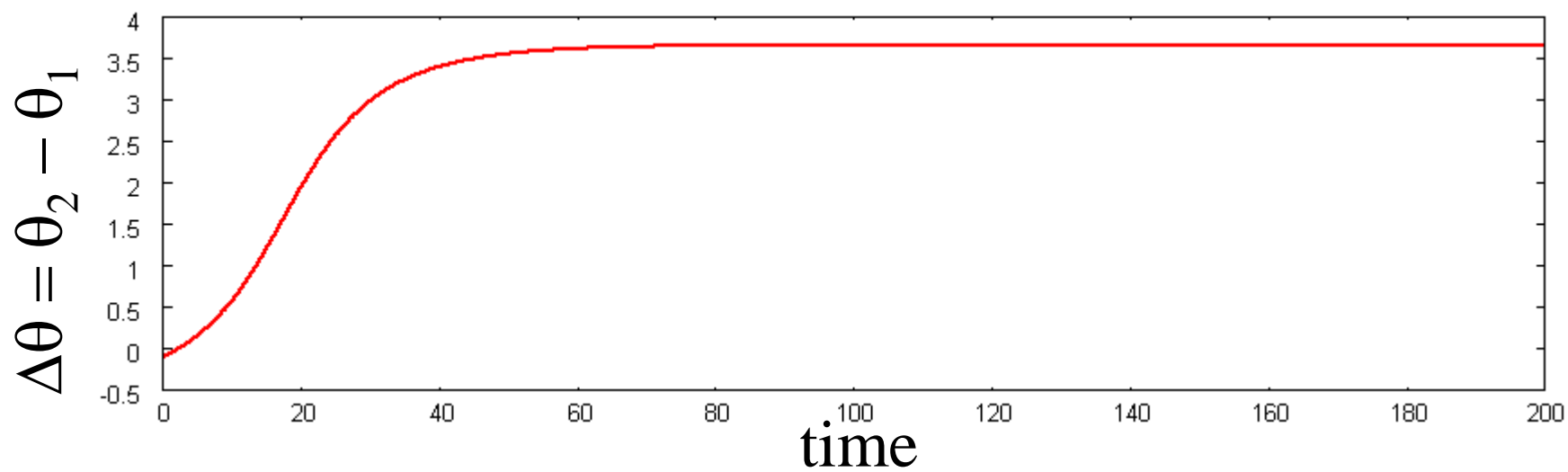
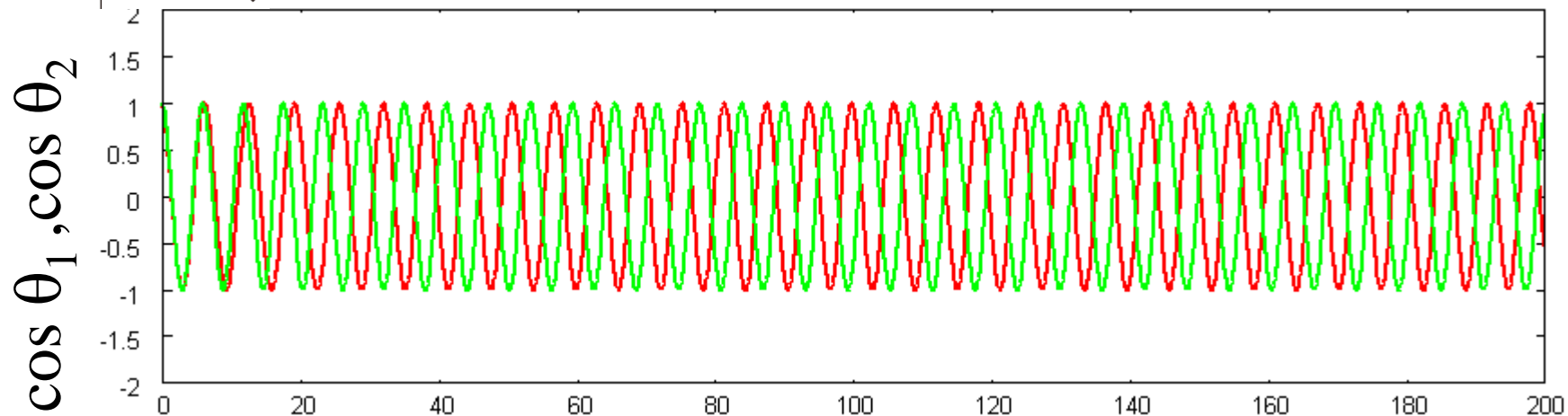


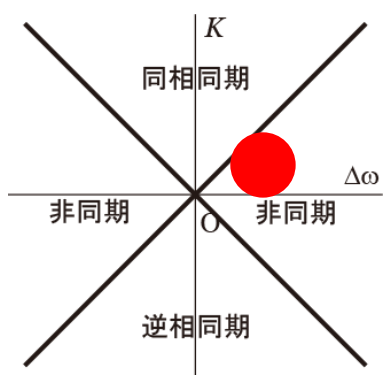


$$\begin{cases} \frac{d\theta_1}{dt} = \omega_1 + K \sin(\theta_2 - \theta_1) \\ \frac{d\theta_2}{dt} = \omega_2 + K \sin(\theta_1 - \theta_2) \end{cases}$$

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

$$K = -0.05$$

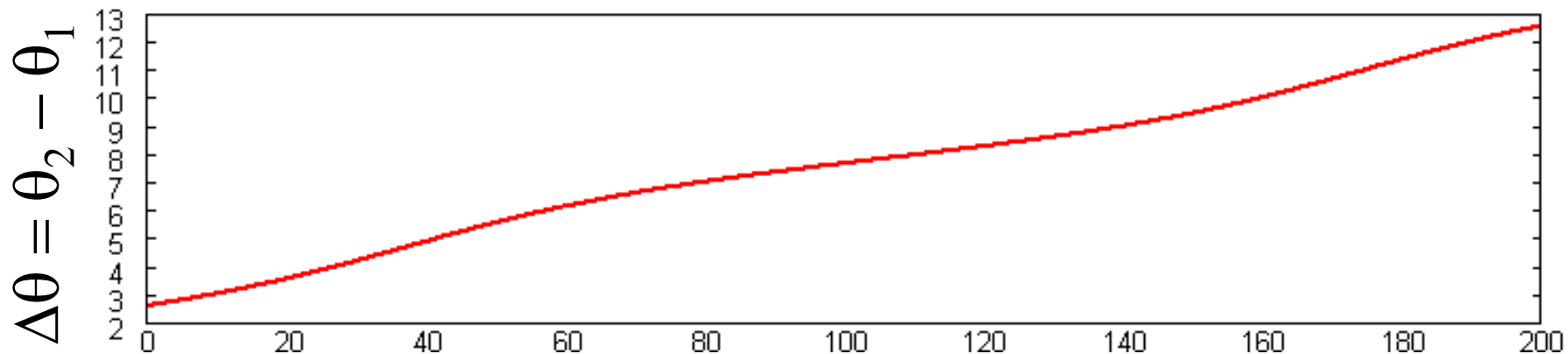
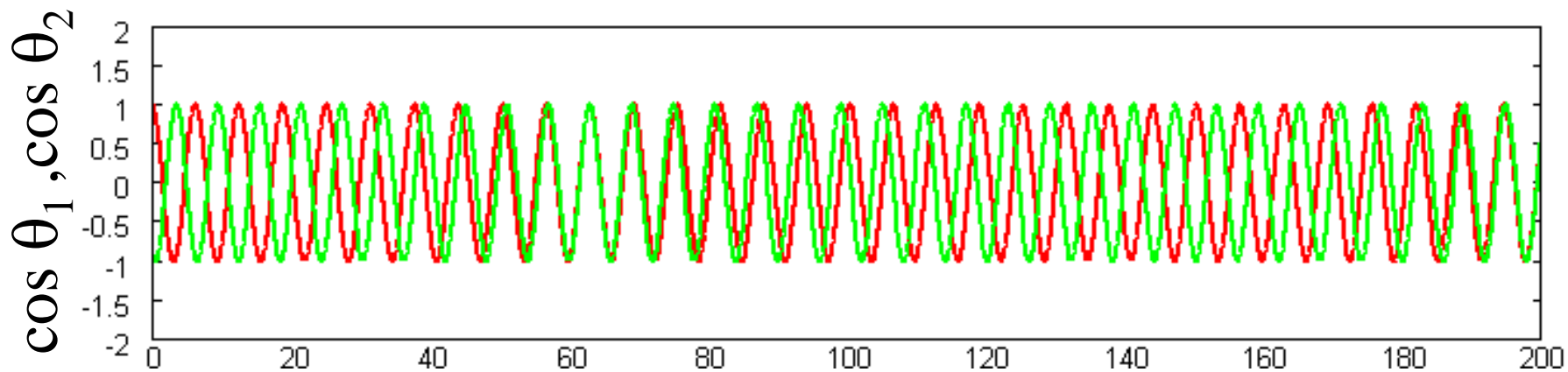




$$\begin{cases} \frac{d\theta_1}{dt} = \omega_1 + K \sin(\theta_2 - \theta_1) \\ \frac{d\theta_2}{dt} = \omega_2 + K \sin(\theta_1 - \theta_2) \end{cases}$$

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

$$K = 0.01$$



time