Belousov - Zhabotinski reaction

$$BrO_3^- + MA \xrightarrow{Ce^{4+}(z)} Br^-\ (y),\ HBrO_2\ (x)$$

$$HOOC-CH_2-COOH$$

BrO_3^- (a) MA (b)

Kinetic equations → dimensional $0 < f < 1$ bifurcation parameter
(a, x, y, z) $q = 0.0008$

$$\begin{cases} \delta \dot{y} = -qay - xy + fbz \\ \varepsilon \dot{x} = ax - x^2 + qay - xy \\ \dot{z} = ax - bz \\ \alpha \dot{a} = \dfrac{x^2}{2} - ax - qay \end{cases}$$

very fast $\delta = 0.0006$
intermediate $\varepsilon = 0.12$ time constants
$= 1$
very slow $\alpha = 73$

$\delta \dot{y} \approx \varepsilon \dot{x} \approx \dot{z} \approx \alpha \dot{a}$ same order of magnitude

$\delta \ll \varepsilon < 1 \ll \alpha$

$$\boxed{\dot{y} \gg \dot{x} > \dot{z} \gg \dot{a}}$$

(I) Hopf : 4 eqs. → 2 eqs.

(II) null-cline method → some features of the oscillations

(III) oscillations vanish

(I) • very slow mode → that mode is suppressed ⇒ $\dot{a} = 0$ ⇒ $a = \text{const}$

pool chemical approximation $\left\{ \begin{array}{l} b = \text{const} \\ a = \text{const} \end{array} \right.$

→ 3 eqs

• pseudo steady state approximation for very fast modes

→ $\dot{y} = 0$ ⇒ $y = \dfrac{fbz}{x + qa}$ $[Br^-]$

→ 2 eqs $y = y(x, z)$

(1)

$$\varepsilon \dot{x} = ax - x^2 - fbz\,\frac{x-qa}{x+qa} = F$$

$[HBrO_2]$

$$\dot{z} = ax - bz = G$$

$[Ce^{4+}]$

2D – Oregonator

$$\alpha \dot{a} = \frac{x^2}{2} - ax - \frac{fbqaz}{x+qa}$$

very slow

Steady states $\quad \dot{x} = 0 = \dot{z} \;\Rightarrow\; (x_s, z_s)$

$$x_s = a\phi \qquad z_s = \frac{a}{b} x_s = \frac{a^2}{b}\phi$$

$\cancel{\phi = 0}$ s.s., not interesting

$$\phi = \frac{1}{2}\left\{ (1-q-f) \pm \sqrt{(1-q-f)^2 + 4q(1+f)} \right\}$$

$\cancel{\ominus \Rightarrow \phi < 0}$

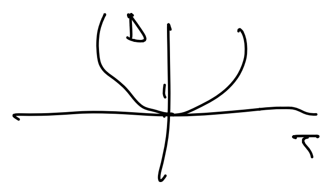
$\boxed{\oplus \Rightarrow \phi > 0}$

$$\phi = \phi(f,q)$$

Is (x_s, z_s) stable? $\quad \Rightarrow \quad \underline{\underline{J}}\big|_s \longrightarrow \operatorname{tr} \underline{\underline{J}} = T$

$$|\underline{\underline{J}}| = D$$

$$\underline{\underline{J}}\Big|_s = \begin{bmatrix} F_x & F_z \\ G_x & G_z \end{bmatrix} \Rightarrow \left|\underline{\underline{J}}\right|\Big|_s > 0 \;!!$$



$$\operatorname{tr} \underline{\underline{J}}\Big|_s = \frac{a}{\varepsilon}\left(1 - 2\phi - \frac{2f\phi q}{(\phi+q)^2}\right) - b \gtrless 0$$

then (x_s, z_s) is unstable

$$\boxed{\frac{b}{a} \leq \frac{1}{\varepsilon}\left(1 - 2\phi - \frac{2f\phi q}{(\phi+q)^2}\right) = \psi(f,q)}$$

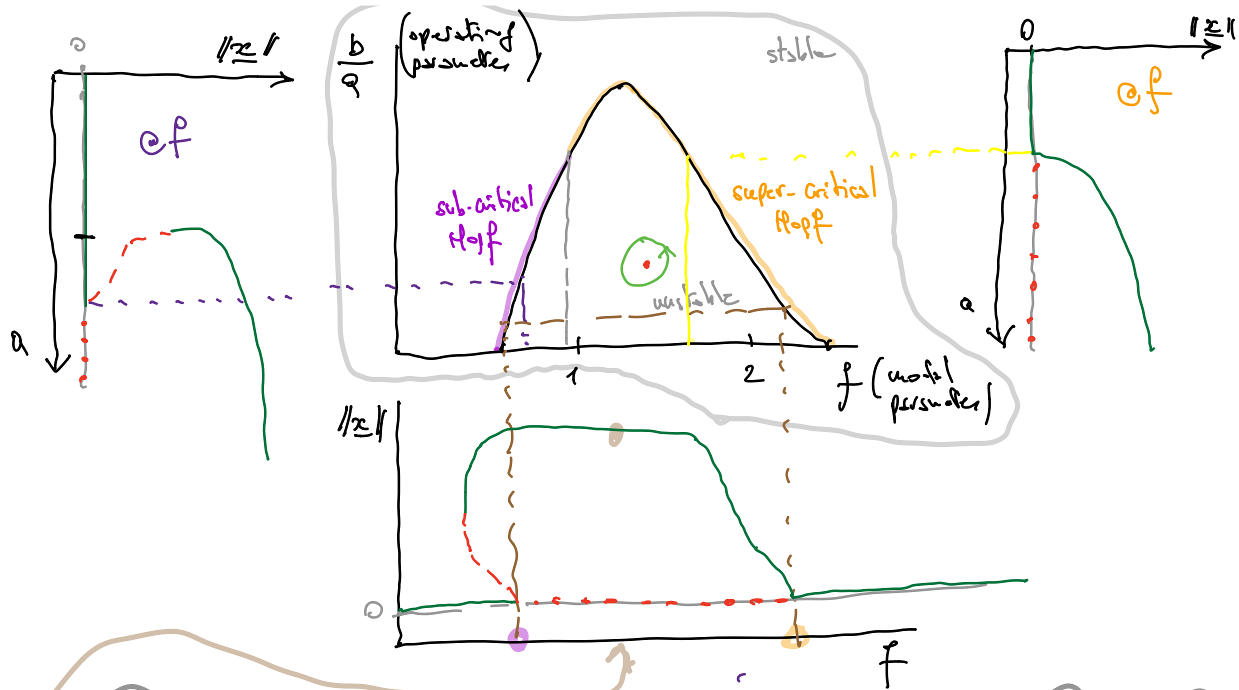
Hopf bifurcation theorem (w.r.t. μ, bifurcation parameter)

(i) s.s. for $\mu = \mu_0$

(ii) $\operatorname{tr}(\underline{\underline{J}}_s) = 0 \quad \mu = \mu_0$

(iii) $\displaystyle \frac{d \operatorname{tr}(\underline{\underline{J}}_s)}{d\mu}\Bigg|_{\mu_0} \neq 0$

$$\boxed{\frac{d \operatorname{tr} \underline{\underline{J}}_s}{da} = \frac{1}{\varepsilon}\left(1 - 2\phi - \frac{2f\phi q}{(\phi+q)^2}\right) = \frac{b}{a} > 0}$$



(II)

2D - Oregonator

faster $\quad \varepsilon \dot{x} = ax - x^2 - fbz\,\frac{x-qa}{x+qa}$

slower $\quad \dot{z} = ax - bz$

$\varepsilon = 0.12$

$= 1$

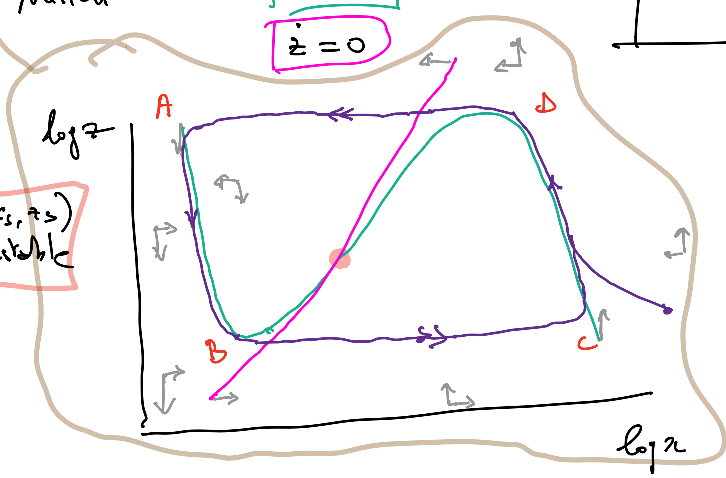
$y = \frac{fbz}{x+qa}$

$z = f(x)$

Nullclines $\quad \dot{x} = 0$

$\dot{z} = 0$

$\boxed{z = \frac{ax}{b}}$



@ (x_s, z_s) is unstable

$\dot{z} \geq 0 \qquad z \leq \frac{a}{b} x$

$\dot{x} \geq 0 \qquad z \leq \frac{(ax - x^2)(x+qa)}{fb(x-qa)}$

$$\begin{cases} \delta \dot{y} = -qay - xy + fbz & \text{very fast} \\ \varepsilon \dot{x} = ax - x^2 + qay - xy & \text{intermediate} \\ \dot{z} = ax - bz & \text{slower} \end{cases}$$

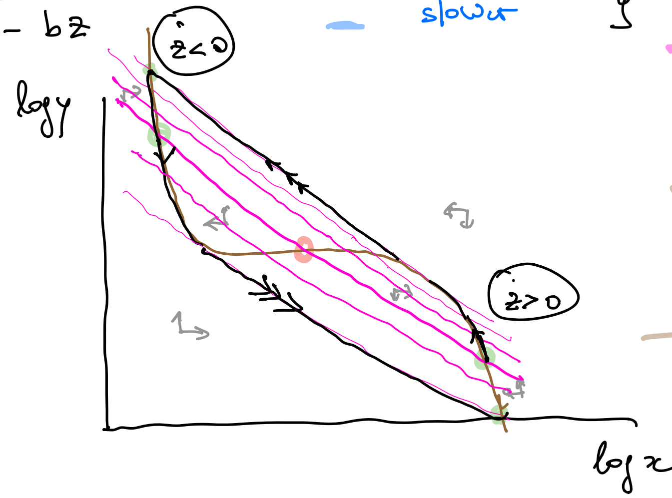
fast subsystem → equilibrium

slow subspace → evolves slowly

$\dot{y} \geq 0 \quad y \leq \dfrac{fbz}{x+qa}$

$\dot{z} \geq 0 \quad y \leq \dfrac{x(a-x)}{x-qa}$

@ z



demonstration of relaxation oscillations

(II)

$$\begin{cases} \delta \dot{y} = -qay - xy + fbz & \text{very fast} \\ \varepsilon \dot{x} = ax - x^2 + qay - xy & \text{intermediate} \\ \dot{z} = ax - bz & \\ \alpha \dot{a} = \dfrac{x^2}{2} - ax - qay & \text{very slow} \end{cases}$$

→ pseudo steady state

$y = \dfrac{fbz}{x+qa}$

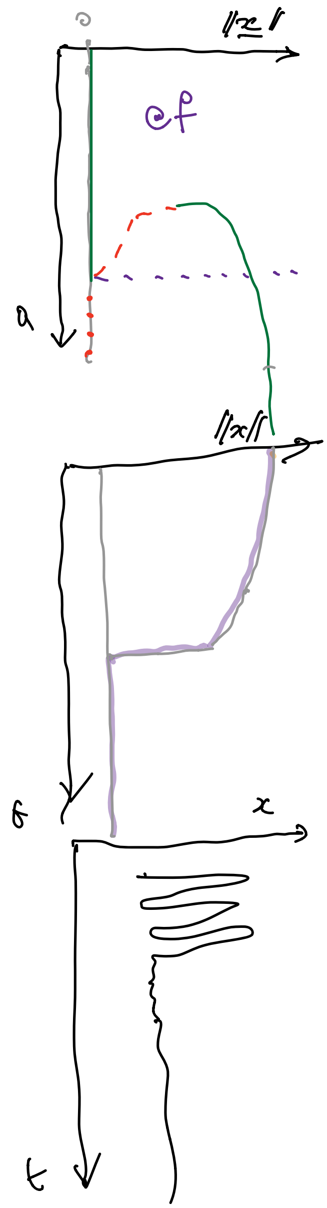
$$\begin{cases} \varepsilon \dot{x} = ax - x^2 - fbz \dfrac{x-qa}{x+qa} & \text{faster} \\ \dot{z} = ax - bz & \text{intermediate} \\ \alpha \dot{a} = \dfrac{x^2}{2} - ax - \dfrac{fbqaz}{x+qa} & \text{very slow} \end{cases}$$

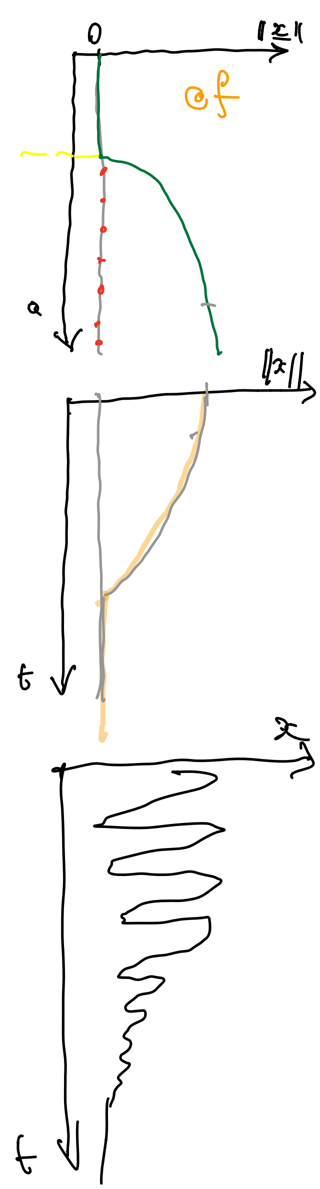
2D Oregonator

$[A] = [BrO_3^-]$

sub-critical Hopf

super-critical Hopf





with O_2

without O_2

exps !!