Nonlinear Oscillation and Multiscale Dynamics in a Closed Chemical Reaction

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Oscillatory Chemical Reaction

History.

Systems of Chemical Reaction

Mathematical Modeling

Main Results

Closed System – The Second Law of Thermodynamics
Far-from-equilibrium Dynamics in $\mathcal{T}^o$
Near-equilibrium Dynamics in $\mathcal{T}^n$
Dynamical Transition from $\mathcal{T}^o$ to $\mathcal{T}^n$

Canonical vs Grand Canonical Systems

Future Work
History

- G.T. Fechner, et al. (1828-1900)
- V. Volterra (1926)
- B. Belousov (1951)
- A.M. Zhabotinsky (1961)
- Ilya Prigogine and his Brussels school

BZ reaction—chemical reaction exhibiting oscillatory behavior.
Systems of Chemical Reaction

- Open system
  Exchange of both molecules and energy with the surroundings is allowed. (for *in vivo* studies)

- Closed system
  Exchange of energy but NOT molecules with the surroundings is allowed. (for *in vitro* studies)

Most of currently existing reaction models exhibiting oscillation are open system.
Irreversible Lotka-Volterra Model

- Irreversible Reaction:
  \[ A + X \xrightarrow{k_1} 2X, \quad X + Y \xrightarrow{k_2} 2Y, \quad Y \xrightarrow{k_3} B, \quad (1) \]

- By the Law of Mass Action, one has

  \[
  \begin{align*}
  \dot{c}_A &= -k_1 c_A x \\
  \dot{x} &= k_1 c_A x - k_2 xy \\
  \dot{y} &= k_2 xy - k_3 y \\
  \dot{c}_B &= k_3 y.
  \end{align*}
  \quad (2)
  \]

  \[
  \begin{align*}
  \dot{x} &= k_1 c_A x - k_2 xy \\
  \dot{y} &= k_2 xy - k_3 y.
  \end{align*}
  \quad (3)
  \]
Reversible Lotka-Volterra System

Reversible Reaction.

\[ A + X \xrightleftharpoons[k_{-1}]{k_1} 2X, \quad X + Y \xrightleftharpoons[k_{-2}]{k_2} 2Y, \quad Y \xrightleftharpoons[k_{-3}]{k_3} B. \] (4)
Reversible Lotka-Volterra System

- Reversible Reaction.

\[ A + X \overset{k_1}{\underset{k_{-1}}{\rightleftharpoons}} 2X, \quad X + Y \overset{k_2}{\underset{k_{-2}}{\rightleftharpoons}} 2Y, \quad Y \overset{k_3}{\underset{k_{-3}}{\rightleftharpoons}} B. \quad (4) \]

- Rate Equations

\[
\begin{align*}
\frac{dx}{dt} &= k_1 c_A x - k_{-1} x^2 - k_2 xy + k_{-2} y^2, \\
\frac{dy}{dt} &= k_2 xy - k_{-2} y^2 - k_3 y + k_{-3} c_B, \\
\frac{dc_A}{dt} &= -k_1 c_A x + k_{-1} x^2, \\
\frac{dc_B}{dt} &= k_3 y - k_{-3} c_B.
\end{align*}
\]  

(5)
Nondimensionalization

- Rescaling

\[
\begin{align*}
    u &= \frac{k_2}{k_3} x, \quad v = \frac{k_2}{k_3} y, \quad w = \frac{k_1}{k_3} c_A, \quad z = \frac{k_2}{k_3} c_B, \quad \tau = k_3 t, \\
    \sigma &= \frac{k_1}{k_2} \ll 1, \quad \frac{k_1}{k_2} = \frac{k_2}{k_2} = \frac{k_3}{k_3} = \varepsilon \ll \sigma.
\end{align*}
\]

- Dimensionless Form.

\[
\begin{align*}
    \frac{du}{d\tau} &= u(w - v) - \varepsilon(\sigma u^2 - v^2) \\
    \frac{dv}{d\tau} &= v(u - 1) - \varepsilon v^2 + \varepsilon z \\
    \frac{dw}{d\tau} &= -\sigma(wu - \varepsilon\sigma u^2). \\
    \frac{dz}{d\tau} &= v - \varepsilon z.
\end{align*}
\]

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Closed System

- **Linear Conservation Law.**
  \[ u + v + \frac{w}{\sigma} + z = \xi = \text{constant}. \]

- **Reduced system.**
  \[
  \begin{align*}
  \frac{du}{d\tau} &= u(w - v) - \varepsilon(\sigma u^2 - v^2) \\
  \frac{dv}{d\tau} &= v(u - 1) - \varepsilon v^2 + \varepsilon \left( \xi - u - v - \frac{w}{\sigma} \right) \\
  \frac{dw}{d\tau} &= -\sigma(\xi - u - v - \frac{w}{\sigma}) \\
  \end{align*}
  \] (8)
Denote
\[ \mathcal{T} = \left\{ (u, v, w) \in \mathbb{R}^3, u, v, w > 0, \text{ and } u + v + \frac{w}{\sigma} \leq \xi \right\}. \]

Then \( \mathcal{T} \) is positively invariant under the flow induced by the closed system (8), and \( \mathcal{T} \) is called the reaction zone.

System (8) has a unique interior equilibrium point \( P \in \mathcal{T} \) at which its Jacobian matrix has three real eigenvalues
\[
|\lambda_1 + (1 + \varepsilon)| \sim \varepsilon^2, \quad |\lambda_2 + \varepsilon \xi| \sim \varepsilon^2, \quad |\lambda_3 + \sigma \varepsilon^2 \xi| \sim \sigma^2 \varepsilon^3.
\]

Thus \( P \) is an asymptotically stable node.
The Second Law of Thermodynamics

$P$ is the global attractor of system (8) in $\mathcal{T}$. The free energy

$$L = u \ln \left( \frac{u}{u^*} \right) + v \ln \left( \frac{v}{v^*} \right) + \frac{w}{\sigma} \ln \left( \frac{w}{w^*} \right) + \left( \xi - u - v - \frac{w}{\sigma} \right) \ln \left( \frac{\xi - u^* - v^* - \frac{w^*}{\sigma}}{\xi - u^* - v^* - \frac{w^*}{\sigma}} \right)$$

serves as the Lyapunov function, where $P = (u^*, v^*, w^*)$. 

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Far-from-equilibrium – Oscillation Zone

There exist $\mathcal{T}^o \subset \mathcal{T}$ and a 1D curve $W^o_{\sigma, \varepsilon} \subset \mathcal{T}^o$ such that all the oscillatory solutions in $\mathcal{T}^o$ go around $W^o_{\sigma, \varepsilon}$. The total oscillation time is $T_o \sim -\frac{\ln \sigma}{\sigma}$. For fixed $w_0 > w_1$, there are at least $N$ complete oscillations by $2\pi$ with $w$ decreasing from $w_0$ to $w_1$, where $N \geq \frac{\ln w_0 - \ln w_1}{2\sigma K} - 1$. And $W^o_{\sigma, \varepsilon}$ is approximately given by

$$W^o_{\sigma, \varepsilon} \sim \left\{(u, v, w), \quad u = \frac{1}{1+\sigma}, \quad v = w, \quad w \in [w, \bar{w}]\right\}.$$
Consider the partially perturbed system where $\varepsilon = 0$

\[
\begin{align*}
\dot{u} &= u(w - v) \\
\dot{v} &= v(u - 1) \\
\dot{w} &= 0
\end{align*}
\Rightarrow \begin{align*}
\dot{u} &= u(w - v) \\
\dot{v} &= v(u - 1) \\
\dot{w} &= -\sigma w u
\end{align*}
\]

which admits a stable invariant manifold

\[
W^o_{\sigma, \varepsilon} = \left\{ (u, v, w), \quad u = \mu_\sigma = \frac{1}{1 + \sigma}, \quad v = w \geq 0 \right\}.
\]

with Lyapunov function

\[
E_\sigma = (1 + \sigma) \left[ u - \mu_\sigma - \ln \left( \frac{u}{\mu_\sigma} \right) \right] + \left[ v - w - w \ln \left( \frac{v}{w} \right) \right]
\]
Normal Hyperbolicity of $W^0_\sigma$?

- **Generalized Lyapunov Type Numbers**
  \[
  \gamma_L(W^0_\sigma) = \lim_{t \to -\infty} \left\| \pi_p^N D\phi_t(W^0_\sigma) \right\|^\frac{1}{t} < 1,
  \]
  \[
  \sigma_L(W^0_\sigma) = \lim_{t \to -\infty} \frac{\log \| D\phi_t(W^0_\sigma) \pi^T_p \|}{\log \| \pi_p^N D\phi_t(W^0_\sigma) \|} \geq 2,
  \]

- **Exponential Dichotomy**
  \[
  u \to \mu_\sigma + x, \quad v \to v + w, \quad w \to w, \quad X = (x, y)^T
  \]
  \[
  \sigma X' = A_\sigma(w)X + G_{\sigma, \varepsilon}(X, w)
  \]
  \[
  w' = F_{\sigma, \varepsilon}(X, w),
  \]
  \[
  A_\sigma(w) = \begin{bmatrix}
  0 & -\mu_\sigma \\
  \frac{w}{\mu_\sigma} & -\sigma \mu_\sigma
  \end{bmatrix}
  \]
  \[
  \text{where } \text{Re}(\lambda(A_\sigma)) \leq -\frac{\sigma \mu_\sigma}{2} \text{ as } w \geq \frac{\sigma^2 \mu_\sigma^2}{4}.
  \]
Proof–Sakamoto (1990)

- Modified system

\[
\begin{align*}
\sigma X' &= A_\sigma(w)X + G_{\sigma,\varepsilon}(X, w) \\
 w' &= F_{\sigma,\varepsilon}(X, w)\chi_{[\sigma^2, \sigma \xi]}(w)
\end{align*}
\]  

(11)

- \[
\begin{align*}
X(t) &= \frac{1}{\sigma} \int_{-\infty}^{t} \Phi_\sigma(t, s, w(s))G_{\sigma,\varepsilon}(X, w)ds \\
w(t) &= H(\eta, X)(t) < \infty, \quad w(0) = \eta \in [\sigma^2, \sigma \xi].
\end{align*}
\]

- \[
\mathcal{F}(X) = \frac{1}{\sigma} \int_{-\infty}^{t} \Phi_\sigma(t, s, H(\eta, X)(s))G_{\sigma,\varepsilon}(X, H(\eta, X)(s))ds.
\]

- \(\mathcal{F}\) is a contraction as \(|X| \leq \delta\) for some \(\delta \Rightarrow \mathcal{F}(X^*_\eta) = X^*_\eta\).

- \(W_{\sigma,\varepsilon}^0 = \{(u = \mu_\sigma + x^*_w(0), v = w + y^*_w(0), w), w \in [\sigma^2, \sigma \xi]\}\).
Define
\[ T_1^o = \{(u, v, w) \in \mathcal{T} : w \geq \sigma\}, \quad T_2^o = \{(u, v, w) \in \mathcal{T} : w \geq \sigma^2\}, \]
\[ \Omega_- = \{(u, v, w) \in \mathcal{T} : v < w\}, \quad \Omega_+ = \{(u, v, w) \in \mathcal{T} : v > w\}. \]

For \( \varepsilon \ll \sigma \ll 1 \) and some \( 1 < \alpha < 2 \),
- \( T_1^o \subset \mathcal{T}^o \subset T_2^o \).
- \( \ln \Omega_+ , \frac{w_{2k+1}}{w_{2k}} \sim 1 \) and \( \frac{E_{2k+1}}{E_{2k}} \sim 1 \).
- \( \ln \Omega_- , \frac{w_{2k+2}}{w_{2k+1}} < e^{-\sigma c_1(w_0,E_0)} \) and \( \frac{E_{2k+2}}{E_{2k+1}} < e^{-\sigma c_2(w_0,E_0)} \).
- At the bottom of \( \mathcal{T}^o \) where \( w \sim \sigma^\alpha, \quad E \sim (\alpha - 2)\sigma^\alpha \ln \sigma \).
Near-equilibrium – Non-oscillation Zone

There exist $\mathcal{T}^n \subset \mathcal{T}$ and a 2D strongly stable invariant manifold $M^n_{\sigma, \varepsilon} \subset \mathcal{T}^n$ and a 1D stable curve $W^n_{\sigma, \varepsilon} \subset M^n_{\sigma, \varepsilon}$. The “total time” in $\mathcal{T}^n$ is $T_n \sim -\frac{\ln \varepsilon}{\varepsilon}$. And

$$W^n_{\sigma, \varepsilon} \sim \left\{ (u, v, w), \quad v = \varepsilon \frac{\xi - u}{1 - u}, \quad w = \sigma \varepsilon u, \quad u \in [0, \bar{u}], \bar{u} < 1 \right\}.$$
Existence of $M^n_{0, \varepsilon}$

Under the following transformation

$$u \rightarrow u, \quad v \rightarrow \varepsilon v, \quad w \rightarrow \sigma \varepsilon w.$$ 

system (8) becomes

$$\begin{align*}
\frac{du}{d\tau} &= \varepsilon \left[ u(\sigma w - v) - (\sigma u^2 - \varepsilon^2 v^2) \right] \\
\frac{dv}{d\tau} &= v(u - 1) - \varepsilon^2 v^2 + (\xi - u - \varepsilon v - \varepsilon w) \\
\frac{dw}{d\tau} &= -\sigma u(w - u).
\end{align*}$$

(12)

By Fenichel's Theorem, critical manifold

$$M^n_n = \left\{ (u, v, w), \quad v = \frac{\xi - u}{1 - u}, \quad u, w \in [0, \bar{u}], \bar{u} < 1 \right\}$$

is normally hyperbolic and thus persists under the perturbation.
Existence of $W_{\sigma, \varepsilon}^n$

- **Reduced System**

\[
\begin{align*}
\frac{du}{d\tau_1} &= \frac{\varepsilon}{\sigma} \left[ u(\sigma w - h_{\sigma, \varepsilon}(u, w)) - (\sigma u^2 - \varepsilon^2 h_{\sigma, \varepsilon}^2(u, w)) \right] \\
\frac{dw}{d\tau_1} &= -u(w - u).
\end{align*}
\]

\begin{equation}
(13)
\end{equation}

Critical manifold

\[ W_0^n = \{(u, w), \; w = u \in [u, \bar{u}], 0 < u < \bar{u} < 1 \} \]

is normally hyperbolic and thus persists under the perturbation.
In the Vicinity of Equilibrium $P$

- Stable Invariant manifold may be applied.
- Further Rescaling

\[ u \rightarrow \sigma \varepsilon u, \quad v \rightarrow v, \quad w \rightarrow w, \quad \tau_2 = \frac{\varepsilon}{\sigma} \tau_1. \]

yields

\[
\begin{cases}
\frac{du}{d\tau_2} = u(\sigma w - h_{\sigma,\varepsilon}) - \left(\sigma^2 \varepsilon u^2 - \frac{\varepsilon}{\sigma} h_{\sigma,\varepsilon}\right) \\
\frac{dw}{d\tau_2} = -\sigma^2 u (w - \sigma \varepsilon u).
\end{cases}
\] (14)
Dynamical Transition from $\mathcal{T}^o$ to $\mathcal{T}^n$

The passage of entering the non-oscillation zone $\mathcal{T}^n$ from the oscillation zone $\mathcal{T}^o$ is around the portion of the central axis connecting $W^o_{\sigma,\varepsilon}$ and $W^n_{\sigma,\varepsilon}$. This is exactly where the transition occurs.
Dynamical Transition from $\mathcal{T}^o$ to $\mathcal{T}^n$
A General Network of Chemical Reactions

Consider a system of chemical reactions whose rate equations, by the law of mass action, are given by

$$X' = V(X) = AR(X)$$  \hspace{1cm} (15)

where $A = (a_{ij})$ is the stoichiometric matrix and

$$R_i(X) = r_i^f(X) - r_i^b(X)$$

with

$$r_i^f(X) = k_i \prod_{a_{ji} < 0} x_j^{-a_{ji}}, \quad r_i^b(X) = k_{-i} \prod_{a_{ji} > 0} x_j^{a_{ji}}.$$

Rewrite equation (15) as

$$\begin{align*}
X_1' &= F_1(X_1, X_2) \\
X_2' &= F_2(X_1, X_2).
\end{align*}$$  \hspace{1cm} (16)

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Canonical System and Grand Canonical System

- **Canonical System.**
  By the linear conservation law $M_1 X_1 + M_2 X_2 = \xi$, equation (16) is reduced into

  $$X'_1 = F_1 (X_1, M_2^{-1} (\xi - M_1 X_1)) .$$  \hspace{1cm} (17)

- **Grand Canonical System.**
  By treating $X_2 = X_2^0$ as a constant vector, equation (16) is reduced into

  $$X'_1 = F_1(X_1; X_2^0).$$  \hspace{1cm} (18)
(Gibb’s Principle) For given $X_2^0$ and $\xi$, let $X_c^*$ and $X_{gc}^*$ be the equilibrium points of systems (17) and (18), respectively. If $X_2^0 = M_2^{-1}(\xi - M_1 X_c^*)$, then $X_c^* = X_{gc}^*$.

- Systems (17) and (18) share the “same” Lyapuov functions.

- Both $X_c^*$ and $X_{gc}^*$ are all asymptotically stable nodes.
Recall
\[
\begin{align*}
\frac{du}{d\tau} &= u(w - v) - \varepsilon(\sigma u^2 - v^2) \\
\frac{dv}{d\tau} &= v(u - 1) - \varepsilon v^2 + \varepsilon z \\
\frac{dw}{d\tau} &= -\sigma(wu - \varepsilon \sigma u^2) \\
\frac{dz}{d\tau} &= v - \varepsilon z.
\end{align*}
\] (19)

Canonical
\[
\begin{align*}
\frac{du}{d\tau} &= u(w - v) - \varepsilon(\sigma u^2 - v^2) \\
\frac{dv}{d\tau} &= v(u - 1) - \varepsilon v^2 + \varepsilon (\xi - u - v - \frac{w}{\sigma}) \\
\frac{dw}{d\tau} &= -\sigma(wu - \varepsilon \sigma u^2) \\
\frac{dz}{d\tau} &= v - \varepsilon z.
\end{align*}
\] (20)

Grand Canonical
\[
\begin{align*}
\frac{du}{d\tau} &= u(w - v) - \varepsilon(\sigma u^2 - v^2) \\
\frac{dv}{d\tau} &= v(u - 1) - \varepsilon v^2 + \varepsilon z \\
\frac{dw}{d\tau} &= -\sigma(wu - \varepsilon \sigma u^2) \\
\frac{dz}{d\tau} &= v - \varepsilon z.
\end{align*}
\] (21)

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System (20) admits similar dynamics as (21) does.
Canonical System vs Grand Canonical System

When $v = v^* \sim \varepsilon$. 

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Future Work

- Effect of noise on the dynamics
  - Macroscopic level– Fokker-Planck equation
  - Microscopic level– chemical master equation (in progress)

- Dissipative perturbation of conserved system.
Thank you!