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Research Paper

Stochastic Models of Two-Species Chemical Oscillators: Fluctuation and Stability

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Abstract: *Oscillatory chemical reactions are of significant importance in chemical and biological sciences. In the present paper we have studied the oscillatory behaviours of two chemical reactions (or oscillators). The first is the classical Lotka model of auto-catalytic chemical reaction and the second is the limit cycle chemical reaction (Tri-molecular reaction) due to Schnakenberg. Beside the deterministic behaviour of stability and bifurcation of the kinetic equations we have studied the stochastic behaviours of fluctuation and stability of the model system under random perturbation which are always present in real conditions.*

Keywords: Chemical Oscillators, Deterministic Models, Random Perturbation, Stochasticity, Fluctuation and Stability.

1. Introduction

Oscillatory phenomena occur in many areas of both living and non-living systems. In bio-chemical and bio-medical sciences they appear in widely varying contexts and have periods from a few seconds to hours and even days and weeks [9]. A large number of recent researches in bio-chemical and bio-medical sciences are concerned with biological oscillators. We have different types of biological oscillators, such as pacemaker oscillator, physiological oscillators, or oscillation in nervous system, chemical oscillators etc [12, 4]. Chemical oscillator is one of the fascinating subjects of biological oscillators [13]. The history of oscillating chemical reactions really dates from Lotka [3]. The extension of this type of analysis for ecological systems leads to the well-known Lotka-Volterra model equations of interacting populations [2]. Over the last four decades many oscillating chemical, specially bio-chemical reactions have been discussed. Among them is the well known and widely studied Belousov-Zhabotinski (simply BZ) reaction [9]. In the spirit of BZ reaction there appeared so

many oscillating chemical reaction systems, for example, Prigogine-Lefever models or brusselators and others [11]. Brusselators are simple examples of limit cycle chemical oscillator [1, 8].

In the present paper we have discussed two oscillating chemical reactions (or chemical oscillators). The first is the classical Lotka model of auto-catalytic chemical reaction along with its ecological significance. The second is the limit-cycle chemical reaction system (or tri-molecular reaction) due to Schnakenberg [10, 7]. We have first studied the deterministic behaviours of stability and bifurcation and then extended these kinetic models to stochastic models by addition of random perturbation terms to the deterministic model equation. The stochasticity arises in view of the many-body aspect of the system. We have studied the stochastic behaviours of fluctuation, stabilities and instabilities of the system under random influences which are always present in real conditions [6].

2. Model Systems: Stochasticity and Fluctuation

Let us consider a system (for example, ecological or chemical reaction) described by a set of n variables $N(t) = (N_1(t), N_2(t),....., N_n(t))$ where $N_i(t)(i = 1,2,..., n)$ is the concentration of the ith component or species at any time t. Let the system is governed by the set of non-linear differential equations

$$\frac{dN_i}{dt} = f_i(N_1, N_2,....., N_n), i = 1,2,....., n \tag{2.1}$$

The system of equations (2.1) being non-linear it is very difficult to solve the system in closed form. In that case it is customary to linearize the system of equations about some stationary state and to study the dynamical behaviours about the stationary state. Let $N^* = (N_1^*, N_2^*,.....N_n^*)$ be a stationary state. We write $x_i = N_i - N_i^*, (i = 1,2,....., n)$ and linearize the system of equations (2.1) about the stationary state $N^* = (N_1^*, N_2^*,.....N_n^*)$ to the form

$$\frac{dx_i}{dt} = \sum_{j=1}^{n} a_{ij} x_j \quad (i = 1,2,....., n) \tag{2.2}$$

where the elements a_{ij} are given by

$$a_{ij} = \left(\frac{\partial f_i}{\partial N_j} \right)_{N^*} \tag{2.3}$$

In matrix form the system of equations (2.2) is written as

$$\frac{dx(t)}{dt} = Ax(t) \tag{2.4}$$

where A is the Jacobian matrix

$$A = \left(a_{ij}\right)_{n \times n} \tag{2.5}$$

and $x(t) = (x_1(t), x_2(t),....., x_n(t))^T$.

We now consider the stochastic extension of the system of equations (2.2). The stochasticity or randomness arises in view of the many-body aspect of the system. We can incorporate this randomness in the system of differential equations (2.2) or (2.4) in the form of the Langevin type of stochastic differential equations

$$\frac{dx(t)}{dt} = Ax(t) + f(t) \tag{2.6}$$

where $x(t)$ is now a random state variable, A is the time-independent drift coefficient and $f(t)$ is the random noise (or perturbation) which is assumed to be a Gaussian white noise satisfying the conditions[6]

$$\langle f(t) \rangle = 0 \; and \; \langle f(t_1) f(t_2) \rangle = 2D\delta(t_2 - t_1) \tag{2.7}$$

where $\langle \; \rangle$ represents the average over the ensemble of the stochastic process and D is the diffusion coefficient or intensity of the random perturbation[6]. The Gaussian white-noise, which is a delta-correlated random process, is very irregular and as such it is to be treated carefully. In spite of this it is an immensely useful concept to model rapidly fluctuating phenomena. Many phenomena of physical and natural systems such as electrical resistance, Brownian particles, climate fluctuation etc are white noises to every good approximation and support the usefulness of the white-noise idealization in applications to chemical and ecological systems [5]. The equation (2.6) is the stochastic extension of first order kinetic equation with a time-independent constant A. It is the basic equation for the study of stochastic fluctuation and stability of the linear stochastic system. The equation (2.6) being a linear differential equation, we conclude

$$x(t) = \int_0^t \varsigma(t,\tau) f(\tau) d\tau \tag{2.8}$$

where $\varsigma(t,\tau)$ is the transfer function of the system satisfying the conditions

$$\begin{aligned} & \varsigma(t,\tau) = 0, \; for \; \tau > t \\ and \quad & \varsigma(\tau.\tau) = 1 \end{aligned} \tag{2.9}$$

which are the physical causality conditions[14]. The function $\varsigma(t,\tau)$ satisfies the differential equation [15]

$$\frac{d\varsigma(t,\tau)}{dt} = A\varsigma(t,\tau) \tag{2.10}$$

The solution of (2.10) is given by

$$\varsigma(t,\tau) = \exp\{-AH(t-\tau)\} \tag{2.11}$$

where $H(x)$ is a Heaviside function of x. Once the transfer function $\varsigma(t,\tau)$ is known, the mean and variance of $x(t)$ at any time t are given by,

$$mean \; x(t) = \langle x(t) \rangle = \int_0^t \varsigma(t,\tau) \langle f(\tau) \rangle d\tau \tag{2.12}$$

$$\text{var}(x(t)) = \sigma^2(t) = \int_0^t \int_0^t \varsigma(t,\tau)\varsigma(t',\tau')\langle f(\tau) f(\tau')\rangle d\tau d\tau' \tag{2.13}$$

Using (2.7), we have,

$$mean\ x(t) = 0 \tag{2.14}$$

$$\sigma^2(t) = \int_0^t \varsigma^2(t,\tau) 2D d\tau \tag{2.15}$$

Differentiating (2.15) w.r.t. time t, and using (2.9) and (2.10) we have

$$\frac{d\sigma^2(t)}{dt} = 2A\sigma^2(t) + 2D \tag{2.16}$$

which is the basic equation of the time-evolution of the variance (or mean-square fluctuation) of the stochastic process $N(t)$.

3. Lotka-Volterra Model System: Stochasticity and Stability

Let us first consider the classical reaction mechanism of autocatalysis proposed by Lotka [3] as a hypothetical model oscillator. The reaction scheme is as follows [9, 3]:

$$A + X \xrightarrow{k_1} 2X, \quad X + Y \xrightarrow{k_2} 2Y, \quad Y \xrightarrow{k_3} B \tag{3.1}$$

where A is maintained at constant concentration a. The first two reactions are autocatalytic. The law of Mass Action gives

$$\frac{dX}{dt} = k_1 aX - k_2 XY$$
$$\frac{dY}{dt} = k_2 XY - k_3 Y \tag{3.2}$$

where X and Y represent also the concentrations of the substances X and Y respectively. In non-dimensional variables

$$x = \frac{k_2 X}{k_3},\ y = \frac{k_2 y}{k_1 a},\ \tau = k_1 at,\ \alpha = \frac{k_3}{k_1 a} \tag{3.3}$$

The system of equations (3.2) reduces to the form

$$\frac{dx}{dt} = x(1-y), \qquad \frac{dy}{dt} = \alpha y(x-1) \tag{3.4}$$

which are the well known Lotka-Volterra system of equations for prey-predator system in population dynamics [9, 3]. The stationary states of the system are $(x^*, y^*) = (0,0)$ and (1,1). The stationary state (0,0) is a saddle point. We are, however, interested in the point (1,1). We write $x = 1 + x',\ y = 1 + y'$ where x' and y' are small deviations from the respective stationary values. Linearizing the system of equations (3.4) about the stationary values we have the linear equation

$$\begin{pmatrix} \frac{dx'}{d\tau} \\ \frac{dy'}{d\tau} \end{pmatrix} = A \begin{pmatrix} x' \\ y' \end{pmatrix} \tag{3.5}$$

where

$$A = \begin{pmatrix} 0 & -1 \\ \alpha & 0 \end{pmatrix} \tag{3.6}$$

is the Jacobian matrix with eigenvalues

$$(\lambda_1, \lambda_2) = \pm i\sqrt{\alpha} \tag{3.7}$$

Since the eigenvalues are purely imaginary, $\mathrm{Re}(\lambda) = 0$ the stationary state (1, 1) is a centre singularity and is neutrally stable. The solution of (3.5) is then given by

$$\begin{pmatrix} x'(\tau) \\ y'(\tau) \end{pmatrix} = v_1 e^{i\sqrt{\alpha}\,\tau} + v_2 e^{-i\sqrt{\alpha}\,\tau} \tag{3.8}$$

where v_1 and v_2 are arbitrary column vectors. The solution (3.8) in the neighbourhood of the singular point (1,1) are periodic in τ with period $\frac{2\pi}{\sqrt{\alpha}}$ or $2\pi\left(\frac{k_1 a}{k_3}\right)^{\frac{1}{2}}$. In the ecological context the Jacobian matrix A given by (3.6) is the community matrix whose eigenvalues λ determines the stability of the stationary states. If $\mathrm{Re}(\lambda) > 0$, the stationary state is unstable while if $\mathrm{Re}(\lambda) < 0$, it is stable. The critical case $\mathrm{Re}(\lambda) = 0$ is termed as neutral stability and structurally unstable [9].

Let us now investigate the behaviour of the system under random perturbation. The equation (3.5) then becomes

$$\begin{pmatrix} \frac{dx'}{d\tau} \\ \frac{dy'}{d\tau} \end{pmatrix} = A \begin{pmatrix} x' \\ y' \end{pmatrix} + \begin{pmatrix} f_1(\tau) \\ f_2(\tau) \end{pmatrix} \tag{3.9}$$

where the random perturbations $f_i(\tau)$ according to (2.7) are white-noise satisfying the conditions

$$\langle f_i(\tau) \rangle = 0 \;\; and \;\; \langle f_i(\tau_1) f_i(\tau_2) \rangle = 2D_i \delta(\tau_2 - \tau_1), \;\; (i = 1,2) \tag{3.10}$$

Taking averages of the both sides of (3.9) and using (3.10) we have the differential equations for the averages

$$\begin{pmatrix} \frac{d\langle x' \rangle}{d\tau} \\ \frac{d\langle y' \rangle}{d\tau} \end{pmatrix} = A \begin{pmatrix} \langle x' \rangle \\ \langle y' \rangle \end{pmatrix} \tag{3.11}$$

According to (2.16) we have the equations of variances (or root-mean square fluctuations)

$$\frac{d}{d\tau}\begin{pmatrix}\langle x'^2(\tau)\rangle\\ \langle y'^2(\tau)\rangle\end{pmatrix} = 2A\begin{pmatrix}\langle x'^2(\tau)\rangle\\ \langle y'^2(\tau)\rangle\end{pmatrix} + 2\begin{pmatrix}D_1\\ D_2\end{pmatrix} \tag{3.12}$$

Then the solution of (3.12) is given by

$$\begin{pmatrix}\langle x'^2(\tau)\rangle\\ \langle y'^2(\tau)\rangle\end{pmatrix} = \underline{L_1}e^{2i\sqrt{\alpha}\,\tau} + \underline{L_2}e^{-2i\sqrt{\alpha}\,\tau} + \underline{M} \tag{3.13}$$

where $\underline{L_1}, \underline{L_2}$ and $\underline{M}$ are constant column vectors. The first and the second terms of (3.13) are periodic with period $\frac{\pi}{\sqrt{\alpha}}$. The third term is a finite constant and is non-zero as long as the intensity of fluctuations D_1, D_2 are non-zero. From the consideration of stochastic stability in the sense of second-order moment the system is not stable. This implies that Lotka-Volterra system is unstable under the influence of a random perturbation whatever small it may be[9].

4. Schnakenberg Model System: Stochasticity and Stability

Schnakenberg[9] considered a class of two species but chemically possible tri-molecular reaction which admits periodic solutions. The simplest of such reaction mechanism is

$$2X + Y \leftrightarrow 3X,\ A \rightarrow Y,\ X \leftrightarrow B \tag{4.1}$$

The concentrations of A and B are externally given and are fixed in time and those of X and Y are variables depending on time. We denote the concentrations of the substances (or species) X, Y, A and B by x, y, a and b respectively. The model equations of the reaction scheme (4.1) are

$$\begin{aligned}\frac{dx}{dt} &= x^2y - x + b = f(x,y)\ (say)\\ \frac{dy}{dt} &= -x^2y + a = g(x,y)\ (say)\end{aligned} \tag{4.2}$$

The stationary state of the system (4.2) is

$$(x_0, y_0) = \left\{(a+b), \frac{a}{(a+b)^2}\right\} \tag{4.3}$$

We write $x = x_0 + x',\ y = y_0 + y'$ and linearizing the system of equations (4.1) about the stationary state we have the linear equations

$$\begin{pmatrix}\frac{dx'}{dt}\\ \frac{dy'}{dt}\end{pmatrix} = A\begin{pmatrix}x'\\ y'\end{pmatrix} \tag{4.4}$$

where the Jacobian matrix A is given by

$$A=\begin{pmatrix}\frac{\partial f}{\partial x} & \frac{\partial f}{\partial y}\\ \frac{\partial g}{\partial x} & \frac{\partial g}{\partial y}\end{pmatrix}_{(x_0,y_0)}=\begin{pmatrix}\frac{a-b}{a+b} & (a+b)^2\\ -\frac{2a}{a+b} & -(a+b)^2\end{pmatrix} \tag{4.5}$$

Then the eigenvalue equation is

$$\lambda^2-\beta\lambda+\gamma=0 \tag{4.6}$$

where

$$\beta=TrA=\frac{a-b}{a+b}-(a+b)^2$$
$$\gamma=|A|=(a+b)^2>0 \tag{4.7}$$

with eigenvalues

$$\lambda_1,\lambda_2=\frac{\beta\pm\sqrt{\beta^2-4\gamma}}{2}=\frac{\beta\pm i\delta}{2} \tag{4.8}$$

where $\delta^2=4\gamma-\beta^2$

The solution of the equation (4.4) is given by

$$\begin{pmatrix}x'\\ y'\end{pmatrix}=\underline{v_1}e^{(\beta+i\delta)t}+\underline{v_2}e^{(\beta-i\delta)t} \tag{4.9}$$

where $\underline{v_1}$ and $\underline{v_2}$ are the constant column vectors. The stationary state (4.3) is then a stable focus if $\beta<0$ i.e. if $(a-b)<(a+b)^3$ and is unstable focus if $\beta>0$ i.e. if $(a-b)>(a+b)^3$. If $\beta=0$ i.e. if $(a-b)=(a+b)^3$ we have then a bifurcation point. This corresponds to the transition of the system from the stable focus $\beta<0$ to the unstable focus $\beta>0$. The eigenvalues corresponding to the bifurcation value $\beta=0$ are then given by

$$\lambda_{1,2}=\pm\frac{\delta i}{2}=\pm(a+b)i \tag{4.10}$$

Let us now investigate the behaviour of the system under random perturbation. The equation (4.4) then becomes

$$\begin{pmatrix}\frac{dx'}{dt}\\ \frac{dy'}{dt}\end{pmatrix}=A\begin{pmatrix}x'\\ y'\end{pmatrix}+\begin{pmatrix}f_1(t)\\ f_2(t)\end{pmatrix} \tag{4.11}$$

where the random perturbation is assumed as before to be a white-noise satisfying the conditions

$$\langle f_i(t)\rangle=0,\quad \langle f_i(t_1)\,f_i(t_2)\rangle=2D_i\delta(t_2-t_1)\qquad (i=1,2) \tag{4.12}$$

Proceeding as before, we have the differential equation of variances or mean square fluctuation as

$$\frac{d}{dt}\sigma^2(t) = \frac{d}{dt}\begin{pmatrix}\langle x'^2(t)\rangle \\ \langle y'^2(t)\rangle\end{pmatrix} = 2A\begin{pmatrix}\langle x'\rangle^2 \\ \langle y'\rangle^2\end{pmatrix} + 2\begin{pmatrix}D_1 \\ D_2\end{pmatrix} \tag{4.13}$$

The solution of (4.13) is given by

$$\underline{\sigma^2(t)} = \begin{pmatrix}\langle x'^2(t)\rangle \\ \langle y'^2(t)\rangle\end{pmatrix} = \underline{L_1}e^{2(\beta+i\delta)t} + \underline{L_2}e^{2(\beta-i\delta)t} + \underline{M} \tag{4.14}$$

where $\beta < 0, \underline{\sigma^2(t)} > \underline{M}$, a finite quantity. So the stationary point is unstable unless $\underline{M}$ is negligibly small. If $\beta > 0, \sigma^2(t) \to \infty$, the stationary point is stochastically unstable.

In the case of bifurcation point $\beta = 0$

$$\gamma_{1,2} = \pm(a+b)i \tag{4.15}$$

The variance or mean square fluctuation becomes

$$\underline{\sigma^2(t)} = \begin{pmatrix}\langle x'^2(t)\rangle \\ \langle y'^2(t)\rangle\end{pmatrix} = \underline{L_1'}e^{2(a+b)it} + \underline{L_2'}e^{-2(a+b)it} + \underline{M'} \tag{4.16}$$

which is periodic except a constant term. In the sense of second-order moment the stability point is stochastically unstable.

5. Conclusion

In the present paper we have studied the dynamical behaviours of two chemical oscillators, namely the classical Lotka [3] auto-catalytic chemical reaction and Schnakenberg tri-molecular chemical reaction system [8]. We have made stochastic extension of the deterministic kinetic equation to have Langevin type of stochastic differential equation and studied the fluctuation and stability of the chemical reactions under the effect of random perturbation. The stochasticity or randomness arises in view of the many-body aspect of the system, that is of the irregular interaction of the large number of molecules constituting the system. Chemical reactions constitute a simple field of applications of stochastic methods. The study of processes on deterministic level in some sense is in complete, since stochastic influences are always present under real conditions [6]. The dynamical behaviour of the model systems changes with the effect of random perturbation of the system. For the Lotka-Volterra system the stationary state which is neutrally stable becomes unstable, the mean square fluctuation (or variance) reduces to a constant term with a periodic background noise. For Schnakenberg model system the stability and instability of the stationary state has been investigated for different values of the parameter including the bifurcation point. For the stochastic extension under random perturbation the mean-square fluctuation for all the parametric values including the bifurcation point reduces to constant values with periodic background leading to the instability of the stationary state of the system.

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