

On Solutions of Reaction-Diffusion Equation for Lotka Scheme

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A solution of reaction-diffusion equation has been obtained for the Lotka scheme when the concentration of the reacting species vary periodically with time according to typical Fourier series. The solution is consistent with that obtained by normal mode analysis.

NORMAL mode analysis has been employed in solving reaction-diffusion equation by Prigogine and Glansdroff¹, Rastogi and Kumar². However, the solution implies simple harmonic motion, if oscillations occur at all. In this method the variable X in the neighbourhood of steady state is written as a function of t in the following form:

$$X = X_0 + x_0 \exp(\omega t) \quad \dots(1)$$

where X_0 is the steady state value of X and x_0 is another constant. If ω is imaginary, the value of X would oscillate around X_0 in a simple harmonic manner. However, experimental results of Rastogi *et al.*³ indicate that the concentration of the oscillating species changes with time according to a Fourier series. It is the purpose of this note to show that the oscillatory solutions are still obtained when $X(t, r)$ is expressed in a more general form (Eq. 2) as compared to Eq. (1) around steady state.

$$X = X_0 + \delta x(t, r) \quad \dots(2)$$

In Eq. (2) $\delta x(t, r)$ is a small perturbation in the neighbourhood of steady state, in both time and space coordinates and which can be expressed as a Fourier series.

Theoretical

The rate equation for species i when both chemical reaction and diffusion occur can be written in the form of Eq. (3)

$$\frac{\partial C_i}{\partial t} = R_i + J_i \quad \dots(3)$$

where C_i is the local concentration of i th species at any time t , R_i is the rate of production of species i and J denotes diffusive flux of the i th component. From Fick's second law of diffusion, the diffusive flux J_i is given by Eq. (4)

$$J_i = D_i \nabla^2 C_i \quad \dots(4)$$

where D_i is the diffusion coefficient of i th component. The Lotka model⁴ chemical oscillator consisting of two sequential autocatalytic reactions may be represented as:



The rate equations are given by Eqs. (6a) and (6b)

$$R_x = k_1 C_A C_x - k_2 C_x C_y \quad \dots(6a)$$

$$R_y = k_2 C_x C_y - k_3 C_y \quad \dots(6b)$$

Therefore, the rate equation for two diffusing-interacting species is described by Eqs. (7a) and (7b)

$$\frac{\partial C_x}{\partial t} = k_1 C_x C_A - k_2 C_x C_y + D_x \nabla^2 C_x \quad \dots(7a)$$

$$\frac{\partial C_y}{\partial t} = k_2 C_x C_y - k_3 C_y + D_y \nabla^2 C_y \quad \dots(7b)$$

where C_A , C_x and C_y denote the concentration of the species A , X and Y for the Lotka system. $\partial C_x / \partial t$ is the rate of accumulation of C_x and ∇^2 is Laplacian operator. All the constants appearing in Eqs. (7a) and (7b) would be positive. In the steady state the concentration of the reactant species are constant in time. The steady state concentration C_x^0 and C_y^0 are given by Eq. (8)

$$C_x^0 = \frac{k_3}{k_2} \text{ and } C_y^0 = \frac{k_1 C_A}{k_2} \quad \dots(8)$$

The concentration of X and Y beyond the steady state at any time t are given by

$$C_x = C_x^0 + \delta x_1 \text{ and } C_y = C_y^0 + \delta x_2 \quad \dots(9)$$

where δx_1 and δx_2 are small perturbations in the system. From Eqs. (7), (8) and (9) the rate equation may be written in matrix notation as follows:

$$\frac{\partial [\delta x]}{\partial t} = (k) [\delta x] + (D) \nabla^2 [\delta x] \quad \dots(10)$$

where

$$[\delta x] = \begin{pmatrix} \delta x_1 \\ \delta x_2 \end{pmatrix}, (K) = \begin{pmatrix} k_1 C_A - k_2 C_y^0 & -k_2 C_x^0 \\ k_2 C_x^0 & k_2 C_x^0 - k_3 \end{pmatrix}$$

$$\text{and } (D) = \begin{pmatrix} D_x & 0 \\ 0 & D_y \end{pmatrix}$$

Eq. (10) simply states that if steady state of the system is slightly perturbed, the rate of change of perturbation is controlled by the rate of the chemical reaction and the diffusion process.

Solutions of the Equation

Eq. (10) can be solved as an eigenvalue problem and the solution can be written as

$$[\delta x] = \sum_{k=-\infty}^{+\infty} [\phi_k(t) f_k(r)] \quad \dots(11)$$

where $f_k(r)$ represents the complete set of eigenfunction of Laplacian part and $[\phi_k(t)]$ the time dependent part. Eigenfunctions of the Laplacian satisfy the relationship

$$\Delta^2 f_k(r) = -k^2 f_k(r) \quad \dots(12)$$

where k is the characteristic eigenvalue corresponding to eigenfunction $f_k(r)$. k describes the wavelength of the oscillations so that the frequency of oscillation would be $2\pi/k$. The eigenfunctions $f_k(r)$ possess the property of orthogonality:

$$\int_s f_k(r) f_j(r) d\tau = \begin{cases} 1 & k=j \\ 0 & k \neq j \end{cases} \quad \dots(13)$$

Using Eqs. (11), (12) and (13) for the transformation of Eq. (10) we have

$$\frac{\partial}{\partial t} [\phi_k] = \{(K) - k^2(D)\} [\phi_k] \quad \dots(14)$$

The solutions of Eq. (14) would be of the form⁵⁻⁷

$$[\phi_k(t)] = \sum_{i=1}^N a_{ki} [A]_{ki} \exp(\lambda_{ki} t) \quad \dots(15)$$

where λ_{ki} are the N eigenvalues, $[A]_{ki}$ corresponds to the N eigenvectors of the matrix $\{(K) - k^2(D)\}$ and a_{ki} are constants. The eigenvalues are the roots of the determinant of the characteristic matrix

$$\det \{(K) - k^2(D) - \lambda(I)\} = 0 \quad \dots(16)$$

where (I) is the identity matrix. Therefore, the general solution of the equation would be given by

$$[\delta x] = \sum_{k=-\infty}^{+\infty} \left\{ \sum_{i=1}^N (a_{ki} [A]_{ki} \exp(\lambda_{ki} t)) f_k(r) \right\} \quad \dots(17)$$

Discussion

By solving Eq. (16) and putting the values of the steady state concentrations from Eq. (8) the eigenvalues are given by Eq. (18)

$$\lambda_{ki} = -\frac{k^2(D_x + D_y)}{2} \pm \frac{1}{2} [k^4(D_y - D_x)^2 - 4k_1 k_3 C_A]^{1/2} \quad \dots(18)$$

and eigenvector

$$\phi_k(0) = \begin{pmatrix} -\lambda_k / C_A k_1 \\ 0 \end{pmatrix}$$

Following conclusions follow from Eq. (18): (a) If the real part of the eigenvalue is negative the solutions would be stable and concentration of X will decay exponentially. (b) If the real part is positive, the system would be unstable because the concentration of X would increase exponentially by the presence of small perturbation. (c) If

$$4 k_1 k_3 C_A > k^4 (D_y - D_x)^2 \quad \dots(19)$$

$$\text{or } k^2 < \frac{2(k_1 k_3 C_A)^{1/2}}{(D_y - D_x)}$$

the eigenvalues λ_{ki} would be imaginary and the system would exhibit oscillatory behaviour.

(d) If $D_x = D_y = D$, the eigenvalues would be given by

$$\lambda_{ki} = -k^2 D \pm i(k_1 k_3 C_A)^{1/2} \quad \dots(20)$$

The system would show oscillatory behaviour, and the frequency of the oscillations would be given by Eq. (2)

$$\omega = \pm \frac{(k_1 k_3 C_A)^{1/2}}{2} \quad \dots(21)$$

Eqs. (19), (20) and (21) are similar to those found by normal model analysis by Rastogi *et al.*²

The formal solutions of Eq. (17) indicates that the oscillatory nature of a reaction system depends on the eigenvalues of the matrix $[(K) - k^2(D)]$, which in turn depends on the reaction rates, diffusion coefficients and the frequency of the oscillations.

The above analysis shows that Lotka scheme admits periodic solutions of reaction-diffusion equation even when the periodicity of oscillations is represented by a Fourier series.

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