

NONLINEAR PHENOMENA IN CHEMICAL KINETICS

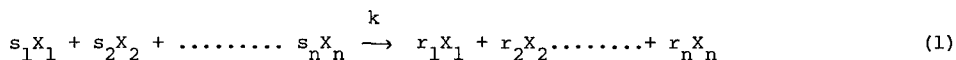
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1. Introduction

Recent years have seen an upsurge of activity in the area of non-linear phenomena in open systems. Numerous phenomena in a wide variety of fields such as hydrodynamics, quantum optics, lasers, electrical networks, ecology, chemical reactions have been investigated by several authors so as to determine features that might be common to all these seemingly diverse systems[1,2]. Indeed this has led to the emergence of a new discipline in physics called Synergetics[1]. Chemical reactions have been of particular interest because one hopes that they might offer a clue to the formation of ordered structures, spatial and temporal oscillations that occur in many biological systems. Main interest in this area has been in setting up simple models which reproduce the essential features of the phenomena observed in nature. Our modest aim in these lectures is to make the uninitiated somewhat familiar with the models and the theoretical techniques used in this area.

2. Chemical Kinetics : Rate Equations :

Consider a chemical reaction involving n chemicals X_1, \dots, X_n taking place in a vessel of volume V



The macroscopic variables of interest are obviously the number of molecules X_i of the chemical X_i . Each time a reaction occurs the number of molecules X_i of type X_i change from X_i to $X_i + r_i - s_i$. The question we ask now is : what are the equations that describe the change in number of molecules of the reactants during the course of a chemical reaction? The answer to this question has been known since the early days of chemical kinetics : The rate at which a chemical reaction occurs is proportional to the product of concentrations of the reactants

$$k \prod_{i=1}^n x_i^{s_i} \quad ; \quad x_i = \frac{X_i}{V} \quad (2)$$

Here k is a constant called the rate constant and involves the cross section for a reactive collision between the reactant molecules. More precisely (2) is the number of collisions per unit time per unit volume in which the number of molecules X_i of type X_i change from X_i before the collision to $X_i + r_i - s_i$. The rate equations are therefore:

$$\frac{dX_i}{dt} = k(r_i - s_i) V \prod_{i=1}^n (x_i)^{s_i} \quad (3)$$

or

$$\frac{dx_i}{dt} = k (r_i - s_i) \prod_i (x_i)^{s_i} \quad (4)$$

These considerations allow us to write down the rate equations for any arbitrary chemical reaction. Thus, for instance, for the reaction



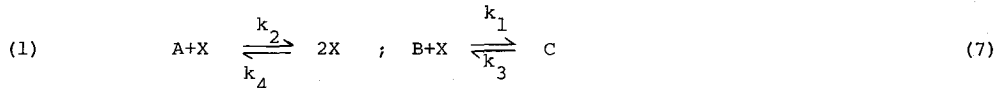
The rate equations are

$$\begin{aligned} \frac{dx}{dt} &= -2k_1 x^2 + 2k_2 y \\ \frac{dy}{dt} &= k_1 x^2 - k_2 y \end{aligned} \quad (6)$$

The above description is valid provided a number of physical requirements are satisfied[3]. It is a good description for an isothermal homogeneous chemical reaction in which Maxwell distribution is maintained through sufficiently frequent non-reactive collisions.

3. Some Examples of Open Chemical Systems Exhibiting Interesting Non-Linear Phenomena:

The reaction (5) considered above is an example of a closed chemical system as it does not involve any flow of matter from outside. The stationary states of such systems do not exhibit anything particularly striking. However a wide variety of interesting phenomena become possible in open chemical systems i.e. chemical systems in which certain chemicals are externally maintained at fixed controllable concentrations. Some examples of such chemical reactions which have been extensively studied in the literature are given below

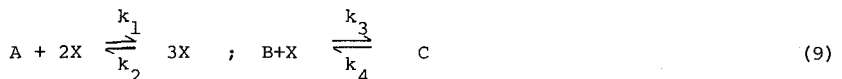


Here the chemicals A,B and C are held at a fixed concentration denoted by a,b and c respectively. This model due to Schlögl[4] is an example of an open chemical system which exhibits a second order phase transition behaviour in the steady state. The rate equation for this model is

$$\frac{dx}{dt} = (k_2 a - k_1 b)x - k_4 x^2 + k_3 \quad (8)$$

from which it follows that in the limit $k_3 \rightarrow 0$, $x=0$ is a stable steady state for $k_2 a < k_1 b$ and for $k_2 a > k_1 b$, $x = (k_2 a - k_1 b) / k_4$ becomes the stable steady state.

(2) A second model also due to Schlögl which exhibits a first order phase transition behaviour is as follows

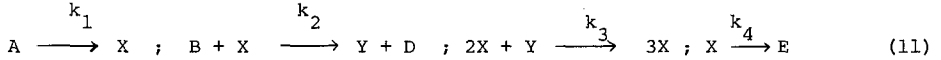


The rate equation for this reaction is

$$\frac{dx}{dt} = k_1 ax^2 - k_2 x^3 - k_3 bx + k_4 c \quad (10)$$

In the steady state one finds that depending on the parameter values one has either one stable steady state or two stable and one unstable steady state.

(3) A two variable example known as the Brusselator[2] which models the oscillations observed in Belusov-Zhabotinsky reaction is as follows :



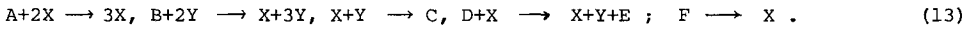
The corresponding rate equations are

$$\frac{dx}{dt} = k_1 a - k_2 bx + k_3 x^2 y - k_4 x$$

$$\frac{dy}{dt} = k_2 bx - k_3 x^2 y \quad (12)$$

A detailed analysis of these equations[2] shows that as one varies the parameter this model exhibits a transition from a homogeneous steady state to a limit cycle behaviour i.e. to sustained temporal oscillations.

(4) Recently Escher[5] has constructed a chemical reaction scheme

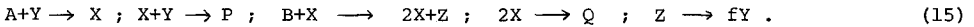


the rate equations for which involve, in contrast to the Brusselator, only quadratic nonlinearities. This model exhibits sustained oscillations on an ellipse in the x-y plane.

We note here that the last three models involve trimolecular reactions which hardly occur in nature. However these reaction schemes are to be understood as effective reaction mechanisms corresponding to a more elaborate reaction system. Thus for instance the trimolecular step in (9) may be thought of as arising from two bimolecular reactions involving a short lived intermediate Y :



Similarly a model called the Oregonator[6] with the same features as the Brusselator but without the trimolecular step is



The rate equations above apply to homogeneous systems. If we drop this requirement and phenomenologically add diffusion terms in accordance with Fick's law then the resulting equations open up possibilities for new kinds of instabilities. For instance, the reaction diffusion equations for the Brusselator

$$\frac{\partial x}{\partial t} = D_x \nabla^2 x + k_1 a - k_2 bx + k_3 x^2 y - k_4 x$$

$$\frac{\partial y}{\partial t} = D_y \nabla^2 y - k_3 x^2 y + k_2 bx \quad (16)$$

exhibit, depending on the parameters, a hard mode instability leading to spatial oscillations [1,2].

Chemical Kinetics : Stochastic Description [7] :

In a stochastic description of a chemical reaction system the question before us is as follows. Given a chemical reaction such as (1) what is the evolution equation for the probability $P(X_1, X_2, \dots, t)$ that at time t we have X_1 molecules of type X_1 , X_2 molecules of type X_2 etc present in the reaction system? Two obvious requirements on such a description are, that one should be able to write down an equation for $P(X_1, X_2, \dots, t)$ from simple kinematic considerations and that this equation should reproduce the macroscopic rate equations in the thermodynamic limit, such a description is known as a mesoscopic description [3]. Let us now outline how one writes an evolution equation - the master equation for $P(X, t)$. As an illustrative example, we consider the reaction



The master equation for (17) must clearly have the following structure

$$\frac{dP(X, t)}{dt} = W(X | X+2) P(X+2, t) - W(X-2 | X) P(X, t) \quad (18)$$

where $W(X | X+2)$ is the transition probability per unit time that $(X+2)$ molecules of X change by 2 to X . We now fix the form of $W(X | X+2)$ from simple combinatorial considerations. Let us divide V into cells of volume ΔV with sides of the order of the interaction range between the molecules. Now clearly

$W(X | X+2) \propto$ (probability that exactly two molecules chosen from $(X+2)$ molecules would find themselves within a cell of volume ΔV somewhere in V) . (no. of ways in which such a pair may be chosen from a total $X+2$ molecules)

$$\begin{aligned} &\propto V \left(\frac{\Delta V}{V}\right)^2 \left(1 - \frac{\Delta V}{V}\right)^X \frac{(X+2)(X+1)}{2!} \\ &= k V \left(\frac{1}{V}\right)^2 (X+2)(X+1) \quad \text{for } \frac{\Delta V}{V} \ll 1. \end{aligned} \quad (19)$$

Hence the master equation for (17) becomes

$$\frac{dP(X, t)}{dt} = kV^{-1} [(X+2)(X+1)P(X+2, t) - X(X-1)P(X, t)] \quad (20)$$

From (20) we have for $\langle x \rangle$, as $V \rightarrow \infty$,

$$\frac{d\langle x \rangle}{dt} = -2k_1 \langle x^2 \rangle \quad (21)$$

If we now heuristically neglect fluctuations by replacing $\langle x^2 \rangle$ by $\langle x \rangle^2$ then we obtain the macroscopic rate equation for (17). A careful analysis based on system size expansion [3] shows that the macroscopic rate equation do indeed emerge from the master equation such as (20) in the thermodynamic limit.

The considerations given above can be easily extended to an arbitrary chemical reaction system. Thus for the reaction system (7) the master equation reads

$$\begin{aligned} \frac{dP(X,t)}{dt} = & k_2 AV^{-1} [(X-1) P(X-1,t) - X P(X-1,t)] \\ & + k_1 BV^{-1} [(X+1) P(X+1,t) - X P(X,t)] \\ & + k_4 V^{-1} [(X+1) X P(X+1,t) - X(X-1) P(X,t)] \\ & + k_3 C [P(X-1,t) - P(X,t)] \end{aligned} \quad (22)$$

Master equations of the type (20) or (22) go by the name of birth-death master equations.

The above description applies to systems where homogeneity is maintained either externally through stirring or internally through rapid diffusion. When this is not the case we have to incorporate effects of spatial diffusion in our description [8]. To do this we divide the system into cells of volume ΔV with side length l . The cells are labelled by an index i and the number of molecules of a chemical X inside cell i are denoted by X_i . Inside each cell we assume homogeneity so that the reaction is described by a master equation such as (22). We model diffusion as a birth death process in which a molecule is transferred from cell i to cell j with probability per unit time $d_{ij} X_i$ i.e. the probability of transfer from cell i to cell j is proportional to the number of molecules in the cell i . The master equation for the reaction diffusion systems then becomes

$$\begin{aligned} \frac{dP(X)}{dt} = & \sum_{ij} d_{ij} [(X_{i+1}) P(X_1 \dots X_{i+1}, \dots X_{j-1}, \dots X_n, t) \\ & - X_i P(X_1 \dots X_n, t)] + \sum_i \left(\frac{\partial P}{\partial t} \right)_{i, \text{chemical}} \end{aligned} \quad (23)$$

Let us first look at only the diffusion part of (23). It follows from (23) that for $\langle x_i(t) \rangle$ we have

$$\frac{d}{dt} \langle x_i \rangle = \sum_j D_{ij} \langle x_j(t) \rangle \quad (24)$$

$$\text{where } D_{ij} = d_{ij} - \delta_{ij} \sum_k d_{jk} \quad (25)$$

We now look at the continuum limit of (25). Suppose that the centre of the cell i is located at r_i

$$x(r_i, t) = \frac{x_i(t)}{l^3} \quad (26)$$

We further assume that

$$d_{ij} = \begin{cases} 0 & i, j \text{ not nearest neighbours} \\ d & i, j \text{ nearest neighbours} \end{cases} \quad (27)$$

Then in the limit $l \rightarrow 0$, (25) becomes

$$\frac{\partial}{\partial t} \langle x(\underline{r}, t) \rangle = D \nabla^2 \langle x(\underline{r}, t) \rangle; \quad D = dl^2 \quad (28)$$

and we recover the usual diffusion equation.

Systematic Expansion Methods:

For any reaction diffusion system master equations such as (23) are easily written down. However solving them to get some information about the fluctuation, particularly when nonlinearities are present is an altogether different proposition. A large number of methods have been developed to this end [9]. A systematic expansion procedure of wide applicability known as system size expansion has been developed by van Kampen [3] to handle such situations. As this method has been discussed at length by Ananthakrishna in these proceedings we shall not follow this method directly but by first transforming the master equation into a more convenient form using the Poisson representation [8,10,11].

The Poisson representation method is based on expanding the probability distribution in terms of Poisson distributions. Thus in a single variable case one writes

$$P(X, t) = \int d\alpha \, e^{-\alpha} \frac{\alpha^X}{X!} f(\alpha, t). \quad (29)$$

$f(\alpha, t)$ is called the quasi probability distribution. It is easily seen that the moments of $f(\alpha, t)$ are equal to the factorial moments of $P(X, t)$.

$$\langle X^n \rangle_P = \langle \alpha^n \rangle \quad (30)$$

Substituting such an expansion in the master equation for any realistic chemical reaction (i.e. a reaction involving only bimolecular steps) one obtains, on integrating by parts, an exact Fokker-Planck type equation for $f(\alpha, t)$. Thus, for instance, for the master equation (22) we get

$$\begin{aligned} \frac{\partial f(\alpha, t)}{\partial t} = & - \frac{\partial}{\partial \alpha} [k_3 c_V + (k_2 a - k_1 b)\alpha + k_4 V^{-1} \alpha^2] f(\alpha, t) \\ & + \frac{1}{2} \frac{\partial^2}{\partial \alpha^2} [2(k_2 a \alpha - k_4 V^{-1} \alpha^2)] f(\alpha, t) \end{aligned} \quad (31)$$

This in turn may be written more conveniently as a stochastic differential equation (Itô type) as

$$\frac{d\alpha}{dt} = k_3 c_V + (k_2 a - k_1 b)\alpha + k_4 V^{-1} \alpha^2 + \sqrt{2(k_2 a \alpha - k_4 V^{-1} \alpha^2)} \xi(t) \quad (32)$$

where $\xi(t)$ denotes a Gaussian white noise. Defining concentration variables in the Poisson representation as $\eta = \alpha/V$ we get

$$\frac{d\eta}{dt} = k_3 c + (k_2 a - k_1 b)\eta + k_4 \eta^2 + \frac{1}{\sqrt{V}} \sqrt{2(k_2 a \eta - k_4 \eta)} \xi(t) \quad (33)$$

Note that in this representation the fluctuating part automatically turns out to have the correct scaling i.e. it is down by a factor of $1/\sqrt{V}$ compared to the non fluctuating

part. The equation (33) is in a form ideally suited for an expansion in powers of $1/\sqrt{V}$

$$\eta = \eta_0 + \left(\frac{1}{\sqrt{V}}\right)\eta_1 + \left(\frac{1}{\sqrt{V}}\right)\eta_2 + \dots \quad (34)$$

Substituting (34) in (33) and solving for η_i iteratively we can solve for η and hence calculate the moments of $P(X,t)$ to an arbitrary power in $1/V$ in a straight forward systematic way.

For reaction diffusion master equations one generalises (29) to

$$P(\underline{X},t) = \int d\underline{\alpha} \left(\prod_i \frac{\alpha_i^{X_i}}{X_i!} e^{-\alpha_i} \right) f(\underline{\alpha},t) \quad (35)$$

Thus for the reaction diffusion system corresponding to (7) one obtains

$$\begin{aligned} \frac{d\eta_i}{dt} = & \sum_j D_{ij} \eta_j + k_3 c + (k_2 a - k_1 b) \eta_i + k_4 \eta_i^2 \\ & + \frac{1}{\sqrt{\Delta V}} \sqrt{2(k_2 a \eta_i - k_4 \eta_i^2)} \xi_i(t) \end{aligned} \quad (36)$$

where $\eta_i(t) = \frac{\alpha_i}{\Delta V}$ and $\xi_i(t)$ are Gaussian white noise sources

$$\langle \xi_i(t) \rangle = 0 ; \quad \langle \xi_i(t) \xi_j(t') \rangle = \delta_{ij} \delta(t-t') \quad (37)$$

In a continuum notation

$$\eta_i(t) \rightarrow \eta(\underline{r}_i, t), \quad \frac{\xi_i(t)}{(\Delta V)^{\frac{1}{2}}} \rightarrow \xi(\underline{r}_i, t) \quad (38)$$

(37) goes over to

$$\frac{d\eta}{dt} = D \nabla^2 \eta + k_3 c + (k_2 a - k_1 b) \eta + k_4 \eta^2 + \sqrt{(k_2 a \eta - k_4 \eta^2)} \xi(r,t) \quad (39)$$

which may again be solved iteratively by introducing a formal expansion parameter λ

$$\eta = \eta_0 + \lambda \eta_1 + \lambda^2 \eta_2$$

Detailed calculation of single time and two time correlation functions based on these methods may be found in [10-12].

We must mention that all techniques that have been developed so far turn out not to be capable of handling fluctuations near a critical point. They merely tell us that the fluctuations become large near a critical point. Much work needs to be done in developing techniques for dealing with critical fluctuations.

Effect of External Perturbations

Effects of external perturbations stochastic or nonstochastic on chemical reaction systems have attracted much attention in recent years. For instance Tomita and Kai [12] have shown that a periodically driven Brusselator

$$\frac{dx}{dt} = k_1 a - k_2 bx + k_3 x^2 y - k_4 x + \alpha \cos \omega t \quad (40)$$

$$\frac{dy}{dt} = -k_3 x^2 + k_2 bx$$

exhibits chaos. A number of authors have investigated chemical reaction systems on noisy environments which have the effect of making the parameters appearing in the rate equations stochastic. This sometimes leads to what are known as 'noise induced transitions'. For details we refer the reader to ref. [13].

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