

# Nonequilibrium Phase Transitions in Chemical Reactions

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The far from equilibrium steady states of a simple nonlinear chemical system are analyzed. A standard macroscopic analysis shows that the nonlinearity introduces an instability which causes a transition analogous to a thermodynamic second-order phase transition. Fluctuations are introduced into this model through a stochastic master equation approach. The solution of this master equation in the steady state reveals that the system goes into a more ordered state above the transition point. An analogy is drawn with the nonequilibrium phase transition occurring in the laser at threshold.

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## 1. INTRODUCTION

There is currently considerable interest in the behavior of systems far from thermodynamic equilibrium, and in particular the nonequilibrium steady states of such systems. Recent investigations have shown that for certain systems nonlinearities introduce instabilities in these far from equilibrium

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steady states. Further, the behavior of these systems around a point of instability is remarkably analogous to the behavior of systems in thermodynamic equilibrium undergoing a second-order phase transition.

The phenomena of nonequilibrium phase transitions may be viewed in the following manner. In order that the system be maintained away from thermodynamic equilibrium, one requires a continual transfer of energy or matter through the system. That is, the system is open to certain surroundings, which are usually idealized to be large reservoirs. These reservoirs may be an energy source (or "pump") or an energy sink. In the absence of a pumping force the system evolves under the action of the dissipative forces into a steady state of thermodynamic equilibrium, which is a state of maximum entropy. The action of the pumping force is to amplify small fluctuations around the thermal equilibrium and drive the system away from equilibrium. For small values of the pumping force the equations describing the time evolution of the system remain linear. The variables characterizing the system are then said to lie on the thermodynamic branch. A linear system always remains on the thermodynamic branch for arbitrary values of the pumping force.

However, in a nonlinear system a "critical value" of the pumping force is eventually reached at which the system becomes unstable. The instability causes large fluctuations in the system variables which are amplified by the pump and there is a rather abrupt change in the physical properties of the system. The variables no longer lie on the thermodynamic branch but on a new, nonthermodynamic branch. An interesting feature of the transition to this new branch is the accompanying increase in order of the system. This new type of order arising through the amplification of fluctuations far from thermal equilibrium has been termed "order through fluctuations."<sup>(1,2)</sup> The ordered structures formed beyond the instability have been termed "dissipative structures."<sup>(1,2)</sup> Such dissipative structures are characterized by a coherent space-time behavior in contrast to the chaotic behavior of a system near thermal equilibrium. Examples of dissipative structures have been observed experimentally in chemical systems.<sup>(3-5)</sup>

An example of a nonequilibrium phase transition which has been analyzed in great detail is provided by the laser oscillator.<sup>(6-9)</sup> Further examples are the parametric oscillator,<sup>(10)</sup> the harmonic oscillator,<sup>(11)</sup> and the behavior of tunnel diode circuits.<sup>(12)</sup> A discussion on nonequilibrium phase transitions in chemical reactions has recently been given by Schlögl,<sup>(13)</sup> who adopted a macroscopic approach which, though describing the behavior of the mean values of the variables, does not include the effects of fluctuations. We shall include fluctuations in a model chemical reaction using a stochastic analysis which allows us to comment explicitly on the degree of order in the system.

## 2. A NONLINEAR CHEMICAL REACTION

A system consisting of a number of molecules of an intermediate species interacting with large reservoirs of initial and final reactants provides an example of a chemical system far from equilibrium. The subsystem comprising the intermediate species is said to be open with respect to the reservoirs of initial and final reactants. As an example of such a system, we consider the following nonlinear biochemical reaction:



This describes the autocatalytic production of the intermediate X and its subsequent enzymatic degradation, the rate constants for the various reactions being given by the  $k_i$ . Here A and C represent the initial and final reactants and B the free enzyme. These are considered to exist in sufficient concentration that they are relatively unperturbed by fluctuations in the concentration of the intermediate species X.

A certain analogy to the operation of a laser is apparent in the above set of chemical reactions. The autocatalytic reaction described by Eq. (1a) is analogous to the stimulated emission process in the laser. The spontaneous creation of a molecule of species X in Eq. (1b) is directly analogous to the spontaneous emission of a photon in the laser. This analogy is more closely drawn by setting  $k_1 = k_3$  (i.e., the Einstein coefficients for spontaneous and stimulated emission are equal). The reaction (1c) represents an irreversible loss of X from the system corresponding to the loss mechanism for laser light, a process largely dominated by the partially reflecting mirror which allows a finite laser light output. The reverse reaction in Eq. (1a) introduces a nonlinearity which is an essential feature if we are to observe an instability. Such an instability occurs in laser action through the nonlinear character of the interaction of the atoms with the radiation field. (For further reading on the subject of lasers consult the excellent review article of Haken.<sup>(14)</sup>) Similar models of nonlinear chemical reactions have been shown to exhibit an instability, using a macroscopic or mean number approach.<sup>(1,13,15-21)</sup> Stochastic methods have been confined to an analysis of small fluctuations around the steady state, thereby linearizing the system.<sup>(22-27)</sup> It is the aim of this paper to include the effects of finite fluctuations in a nonlinear dissipative system.

In order to include fluctuations, we require an equation of motion for the probability function  $P(x, t)$  that there are  $x$  molecules of species X

at time  $t$ . Using standard techniques (see the excellent review paper by McQuarrie<sup>(28)</sup>), we derive the following Markovian master equation for  $P(x, t)$ :

$$\begin{aligned} \partial P(x, t)/\partial t = & F\{xP(x-1) - (x+1)P(x)\} \\ & + D\{(x+1)P(x+1) - xP(x)\} \\ & + k_2\{(x+1)xP(x+1) - x(x-1)P(x)\} \quad (2) \end{aligned}$$

where we have set  $k_1A = F$  (pump parameter) and  $k_4B = D$  (loss parameter).

It has been pointed out by Nicolis and Prigogine<sup>(22,23)</sup> that the birth-death type of stochastic model employed above is inadequate for describing reactions with widely different time scales characterizing relaxation processes associated with elastic and inelastic (reactive) collisions. In these cases a more detailed phase space analysis must be employed. The equation of motion for the mean number of molecules of  $x$  derived directly from the master equation (2) is

$$d\langle x \rangle/dt = F(\langle x \rangle + 1) - k_2(\langle x^2 \rangle - \langle x \rangle) - D\langle x \rangle \quad (3)$$

In the limit of relatively small fluctuations the variance of  $P(x)$  is small; hence we may approximate  $\langle x^2 \rangle \simeq \langle x \rangle^2$  and write Eq. (3) as

$$dX/dt = F(X + 1) - k_2X(X - 1) - DX \quad (4)$$

where  $X$  is the mean number of  $X$  molecules. For a large value of  $X$  we may approximate  $X + 1 \simeq X$  and  $X(X - 1) \simeq X^2$ , so that Eq. (4) becomes

$$dX/dt = (F - D)X - k_2X^2 \quad (5)$$

This corresponds to the macroscopic equation obtained by Schlögl.<sup>(13)</sup>

The solution to Eq. (5) in the steady state ( $dX/dt = 0$ ) is readily seen to be

$$X = \begin{cases} 0, & F \leq D \\ (F - D)/k_2, & F \geq D \end{cases} \quad (6)$$

We neglect the solution  $X = 0$  for  $F > D$  since it is unstable [see Eq. (8)].

Thus the equation for the mean number predicts a transition from a zero mean number of  $X$  molecules to a finite mean number, where the pumping parameter equals the loss parameter  $F = F_c = D$  (see Fig. 1) (cf. Schlögl<sup>(13)</sup>). This is the behavior of a second-order phase transition. It is analogous to the behavior of a ferromagnet in equilibrium thermodynamics. In a ferromagnet the macroscopic magnetization  $M$  (order parameter analogous to  $X$ ) vanishes for a temperature  $T$  (analogous to  $F$ ) higher than a critical temperature  $T_c$  (analogous to  $F_c$ ). (The analogy is inverted since whereas  $F > F_c$  implies nonzero  $X$ ,  $T > T_c$  implies zero  $M$ .)

It is more closely analogous to the nonequilibrium phase transition in the laser, where the mean number of photons (analogous to  $X$ ) suddenly changes

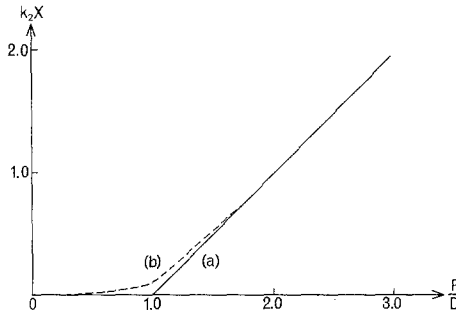


Fig. 1. Plot of the mean number of X molecules against the pumping parameter  $F$ . (a) Macroscopic equation, (b) stochastic equation.

from zero to a finite number when the pumping exceeds the losses. We now show that the critical point  $F = F_c$  is unstable in this macroscopic description. If we add an arbitrary small perturbation  $\delta X$  to  $X$  then,

$$\delta \dot{X} \simeq (\partial \dot{X} / \partial X) \delta X = -(1/\tau) \delta X \quad (7)$$

where  $\tau$  is the regression time for the fluctuation

$$1/\tau = -\partial \dot{X} / \partial X = 2k_2X - (F - F_c) \quad (8)$$

Above and below the critical point,  $\tau$  is strictly positive and finite, so that we have stability. However, at the critical point  $F = F_c$ ,  $\tau$  becomes infinite, so the system becomes unstable. At this point any fluctuations become sufficiently amplified by the pump to cause  $X$  to change from the thermodynamic branch  $X = 0$  to the nonthermodynamic branch  $X = (F - D)/k_2$ . We note that the instability and resultant transition is caused by the nonlinearity introduced by  $k_2$ . For if  $k_2$  is zero, then the solution of Eq. (7) is always the stable solution  $X = 0$ .

### 3. A STATISTICAL DESCRIPTION OF THE STEADY STATE

Though the gross features of the phase transition are described by the mean value analysis, considerably more information may be obtained from a statistical analysis. Thus we shall return to give an exact solution to the stochastic master equation (2) in the steady state. To solve this equation, we invoke the principle of detailed balance, which states (see Fig. 2)

$$FxP(x-1) - (Dx + k_2x(x-1))P(x) = 0 \quad (9)$$

The solution to this first order difference equation is

$$P(x) = P(0) \left( \frac{F}{D} \right)^x \prod_{l=1}^x (1 + \mu l)^{-1} \quad (10)$$

where  $\mu = k_2/D$ .

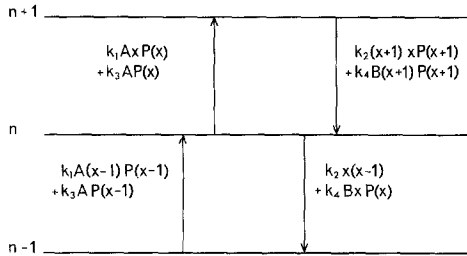


Fig. 2. Flow of probability for finding  $x$  molecules of species X.

Normalization of Eq. (10) gives

$$P(0) = \{ {}_1f_1(1; 1 + 1/\mu; F/D\mu) \}^{-1} \tag{11}$$

where  ${}_1f_1$  is the hypergeometric function.

The mean and second factorial moments of the distribution are, respectively,

$$\langle x \rangle = P(0) \frac{F}{D} \frac{1}{\mu + 1} {}_1f_1\left(2; 2 + \frac{1}{\mu}; \frac{F}{D\mu}\right) \tag{12}$$

$$\langle x(x - 1) \rangle = P(0) \left(\frac{F}{D}\right)^2 \frac{1}{(\mu + 1)(\mu + 2)} {}_1f_1\left(3; 3 + \frac{1}{\mu}; \frac{F}{D\mu}\right) \tag{13}$$

The variance follows immediately from Eqs. (12) and (13).

If we plot the mean number of molecules given by Eq. (12) against the pump parameter  $F$ , we see that there is a sudden increase in the mean number as  $F$  exceeds  $D = F_c$ , similar to the macroscopic result (see Fig. 1). There is, however, a finite number of X molecules produced below threshold, in contrast to the macroscopic result, which predicted zero X molecules below threshold.

A rather more precise understanding of the threshold may be reached by considering the distribution function Eq. (10). For  $F < D$  the  $(F/D)^x$  term ensures that  $P(x)$  decreases rapidly with  $x$  so that the mean is close to zero. For  $F > D$  the nonlinear term involving  $\mu$  causes the distribution to peak away from zero and the mean to become significantly different from zero. A realistic definition of the threshold or critical point is where the distribution first peaks away from zero, that is,  $P(1) = P(0)$ . Applying this condition to Eq. (10) yields  $F = F_c = D(1 + \mu)$ . This differs slightly from the macroscopic result but since the nonlinear parameter  $\mu \ll 1$ , we recover the macroscopic result  $F_c \simeq D$ .

The distribution in the number of X molecules is significantly different above and below threshold.

(a) Below threshold the  $(F/D)^x$  term ensures a rapid decrease in  $P(x)$  with  $x$ , so that the  $(1 + \mu l)^{-1}$  terms never differ appreciably from unity in the region where  $P(x)$  is nonzero. Hence we can write Eq. (10) approximately as

$$P(x) \simeq \left(1 - \frac{F}{D}\right) \left(\frac{F}{D}\right)^x \quad (14)$$

That is, below threshold the number of X molecules obey a geometric distribution. The mean and standard deviation of this distribution are

$$\langle x \rangle = \frac{F}{D} \left(1 - \frac{F}{D}\right)^{-1} \quad (15)$$

$$\sigma = \left(\frac{F}{D}\right)^{1/2} \left(1 - \frac{F}{D}\right)^{-1} \quad (16)$$

We note that macroscopically the mean number of  $F \ll D$  is negligible, agreeing with the macroscopic result  $X = 0$ . However, on a microscopic scale there are considerable fluctuations since the variance of the geometric distribution is large compared to the mean.

(b) Above threshold  $F > D$ . The mean of the distribution (10) can be written in the form

$$\langle x \rangle = \frac{1}{\mu} \left(\frac{F}{D} - 1\right) + \frac{1}{\mu} P(0) \quad (17)$$

Above threshold  $P(0)$  is negligible hence we have

$$\langle x \rangle \simeq (F - D)/k_2 \quad (18)$$

which is the macroscopic result. Far above threshold the distribution is peaked well away from zero; hence we have  $\mu l \gg 1$  and

$$P(x) \simeq e^{-X_0} (X_0)^x / x! \quad (19)$$

where  $X_0 = F/k_2$ , which agrees with the mean given by Eq. (18) for  $F \gg D$ . Equation (19) is a Poisson distribution with mean  $X_0$  and standard deviation  $X_0^{1/2}$ . Since  $X_0 \gg 1$ , we see that the relative fluctuations become much smaller above the critical point.

#### 4. ORDER ABOVE AND BELOW THE CRITICAL POINT

In classical thermodynamics one usually analyzes the behavior of a system around a transition point by examining some suitable macroscopic order parameter which is a measure of the amount of "alignment" or long-range order in the system. For example, in a ferromagnet the order parameter

is taken to be the macroscopic magnetization. The superficial similarity of the mean number of molecules in the chemical system to the magnetization in a ferromagnet suggests that a suitable order parameter for the chemical system is the mean number of species X.<sup>(13)</sup>

This order parameter does not, however, have the immediate physical interpretation of being a measure of alignment in a spatial sense. The non-equilibrium phase transition in the chemical reaction is more directly analogous to the phase transition in the laser at threshold. The order parameter in the laser phase transition is the electric field strength. The number of molecules of species X is directly analogous to the photon number or modulus squared of the electric field strength in the laser.

The behavior of the distribution function  $P(x)$  bears a close similarity with the photon statistics of the laser above and below threshold.<sup>(29)</sup> Below the laser threshold the photons emitted obey a power law distribution typical of a chaotic state.<sup>(30)</sup> This chaotic distribution arises from photons produced by independently emitting atoms. Above threshold the photons emitted in the laser obey a Poisson distribution characteristic of a coherent state.<sup>(30)</sup> This coherent emission is the result of a cooperative behavior or long-range order effect in the laser atoms.<sup>(9)</sup>

By analogy one may postulate that the Poisson distribution in the number of molecules of the chemical species X above threshold reflects a cooperative mechanism for the production of X.

An alternative way of measuring the degree of order in the system is to calculate the entropy of the system. If we take only the variation of species number into account, we may define the statistical form of the entropy as

$$S = - \sum_{x=0}^{\infty} P(x) \log P(x) \quad (20)$$

Below and not too close to the critical point  $P(x)$  is the geometric distribution (14) and the entropy is

$$S \simeq -\frac{F}{D} \log \frac{F}{D} - \log \left( 1 - \frac{F}{D} \right) \quad (21)$$

Far enough above threshold  $P(x)$  is the Poisson distribution (19) and to a good approximation the entropy is

$$S \simeq \frac{1}{2} [\log(2\pi F/k_2) + 1] \quad (22)$$

The absolute value of the entropy increases as a function of the pumping. However, below threshold the entropy  $S$  corresponds to the maximum possible value for a given mean number. That is, the system is in a state of maximum disorder, a characteristic of the thermodynamic branch. Above threshold the



entropy is no longer a maximum, implying that the system has achieved a more ordered state.

## 5. APPLICATIONS AND CONCLUSIONS

We have presented a stochastic analysis of a biochemical system which undergoes a phase transition far from equilibrium to a more ordered state. This is an example of the general concepts put forward by the group of Prigogine and co-workers at Brussels suggesting a mechanism by which chemical and biological systems may evolve to more ordered states indicating an increasing degree of organization. Eigen<sup>(31)</sup> has applied these concepts to give an interpretation of the evolution of "competing" biological molecules toward some type of genetic code.

A possible application of the analysis of the chemical reaction presented in the text is to the problem of muscle contraction recently considered by McClare<sup>(32)</sup> and Markowitz and Nisbet.<sup>(33)</sup> In a model for efficient muscle action the muscle must utilize energy (energy source ATP) at each actin-myosin bridge at approximately the same rate and time as other bridges. That is, there must be some cooperative interaction between the bridges. McClare has introduced this cooperativity by coupling all the bridges in a given thin filament by the  $\alpha$  helix of tropomyosin, which acts as a "waveguide" for transmission of phonons. Thus, "once one A.T.P. has hydrolysed spontaneously the reaction could be made to spread autocatalytically along the thin filament like a controlled explosion."<sup>(32)</sup> This is very close indeed to the situation existing in the chemical reaction (1) above threshold. Similar ideas have been put forward by Shimizu,<sup>(34)</sup> who advanced arguments for considering the ordered motion of motile enzymes as a dissipative structure and applied these concepts to muscle contraction.

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