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Stochastic Models of First-Order Nonequilibrium Phase Transitions in Chemical Reactions

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The steady states of a simple nonlinear chemical system kept far from equilibrium are analyzed. A standard macroscopic analysis shows that the nonlinearity introduces an instability causing a transition analogous to a thermodynamic first-order phase transition. Near this transition the system exhibits hysteresis between two alternative steady states. Fluctuations are introduced into this model using a stochastic master equation. The solution of this master equation is unique, preventing two alternative exactly stable states. However, a quasi-hysteresis occurs involving transitions between alternative metastable steady states on a time scale that is longer than that of the fluctuations around the mean steady state values by a factor of the form $e^{\Delta\phi}$, where $\Delta\phi$ is the height of a generalized thermodynamic potential barrier between the two states. In the thermodynamic limit this time scale tends to infinity and we have essentially two alternative stable steady states.

KEY WORDS: Fluctuations; instabilities; master equations; first-order phase transitions; stochastic processes; nonequilibrium thermodynamics; chemical reactions.

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1. INTRODUCTION

The properties of the far-from-equilibrium steady states of nonlinear systems form the subject of considerable current interest.[2] The possibility of creating a branch of nonequilibrium stationary states in a nonlinear system by driving the thermodynamic branch past an instability has been discussed in detail.(1–4) Such an instability may be symmetry breaking and lead to a new regime with an increase in order. Striking examples of this effect have been shown to occur in laser action(5–8) and in certain autocatalytic chemical reactions.(7–8) These transitions are analogous to second-order phase transitions.

Other instabilities which are not symmetry breaking but involve transitions between two nonequilibrium steady states also arise in certain systems. These transitions may be considered analogous to first-order phase transitions. A discussion of both first- and second-order phase transitions in chemical reactions has been given by Schlögl,(9) who adopted a macroscopic approach. A microscopic treatment of second-order phase transitions in chemical reactions has recently been given by McNeil and Walls.(10) It is the aim of this paper to present a microscopic analysis of a first-order phase transition in a model chemical reaction using a stochastic Markovian master equation approach.

2. A NONLINEAR CHEMICAL REACTION

A chemical system may be kept far from equilibrium if it is open to matter transport with its environment. As an example of such a system, we consider the following nonlinear reaction system:

$$A + 2X \underset{k_2}{\overset{k_1}{\rightleftharpoons}} 3X \tag{1}$$

$$A \underset{k_4}{\overset{k_3}{\rightleftharpoons}} X \tag{2}$$

This describes the conversion of the initial reactant A into X by two different processes: by a simple monomolecular degradation or by an autocatalytic trimolecular mechanism. Both these reactions are reversible, the rate constants for the various reactions being given by the k_i. Here the system is open to interaction with an infinite reservoir of reactant A, so that the concentration of A is kept constant in the reacting system. This might be realized physically in several ways. (1) The reactions occur between rarified gases which are maintained isothermally homogeneous in a stirring vessel which is fed with A so as to keep its concentration constant. (2) The reactions

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[2] Since the completion of this paper, our attention has been drawn to a paper by Nitzan *et al.*,(30) who have independently reproduced some of the qualitative features of our results.

occur in a system where the concentration of X is always much less than that of A, whose concentration is thus effectively undepleted by the reactions.(6) This requires that the reactions be very inefficient in the forward direction. (3) The system is so small that the diffusion of A and X is faster than the reactions between them.

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. We may derive a stochastic master equation for $P(x, t)$ under the Markovian assumption using now standard techniques.(11,12) This yields the following equation:

$$\begin{aligned}\frac{\partial}{\partial t}P(x, t) = {} & [k_1A(x-1)(x-2) + k_3A]P(x-1, t) \\ & - [k_1Ax(x-1) + k_3A + k_2x(x-1)(x-2) + k_4x]P(x, t) \\ & + [k_2x(x-1)(x+1) + k_4(x+1)]P(x+1, t) \qquad (3)\end{aligned}$$

which will be referred to as the master equation.

An exact analytic solution of this master equation in terms of elementary functions does not exist except in the steady state. However, various approximation methods can be used to obtain information about the dynamical behavior of the system.

3. MACROSCOPIC EQUATIONS, STOCHASTIC MEAN VALUES

Equations of motion for the moments of the distribution function $P(x, t)$ can be derived directly from the master equation. The equation of motion for the mean number of X molecules reads

$$\begin{aligned}\frac{\partial}{\partial t}\langle x\rangle = {} & k_1A(\langle x^2\rangle - \langle x\rangle) - k_2(\langle x^3\rangle - 3\langle x^2\rangle + 2\langle x\rangle) \\ & + k_3A - k_4\langle x\rangle \qquad (4)\end{aligned}$$

Neglecting fluctuations, that is, setting $\langle x^2\rangle = \langle x\rangle^2$ and $\langle x^3\rangle = \langle x\rangle^3$, and for $\langle x\rangle \gg 1$, this equation reduces to

$$dX/dt = -k_2X^3 + k_1AX^2 - k_4X + k_3A, \qquad X \equiv \langle x\rangle \qquad (5)$$

which is exactly the macroscopic rate equation for the chemical reactions (1) and (2) derived from the law of mass action.(9) The solution of Eq. (5) with the initial condition $X(0) = X_0$ is

$$\begin{aligned}&\left(\frac{X - X_1}{X_0 + X_1}\right)^{x_3 - x_2}\left(\frac{X - X_2}{X_0 - X_2}\right)^{x_1 - x_3}\left(\frac{X - X_3}{X_0 - X_3}\right)^{x_2 - x_1} \\ &\qquad = \exp\{-k_2(X_1 - X_2)(X_2 - X_3)(X_3 - X_1)t\} \qquad (6)\end{aligned}$$

where X_1, X_2, and X_3 are the roots of

$$k_2X^3 - k_1AX^2 + k_4X - k_3A = 0 \qquad (7)$$

with $X_3 \geqslant X_2 \geqslant X_1$. The macroscopic dynamical behavior described by Eq. (6) has been discussed in Ref. 13.

The steady state solutions of Eq. (6), X^s, are

$$\begin{array}{ll} X_0 < X_2, & X^s = X_1 \\ X_0 = X_2, & X^s = X_2 \\ X_0 > X_2, & X^s = X_3 \end{array} \tag{8}$$

A normal mode analysis of Eq. (6) shows that the solution X_2 is unstable with respect to small perturbations. This will be apparent when fluctuations are included.

This "deterministic" type of analysis predicts the existence of one or three steady states, depending on the parameters that are the coefficients of X in Eq. (7). If we define $k_1A/k_2 = B$, $k_4/k_2 = R$, and $k_3/k_1 = P$, then P and R are determined by the details of the reaction mechanisms of reactions (1) and (2) whereas B is determined by A and will be referred to as the pump parameter. The dependence of X on B is illustrated in Fig. 2 for various values of R and P. The case of $P = R$ means that the net rates of reactions (1) and (2) separately vanish, and a true chemical equilibrium exists with $X = B$.

It is also apparent from Eq. (8) that a hysteresis in X may occur as X is varied; if B is increased starting from zero (see Fig. 3), the steady state on the lower branch OP_1 eventually coincides with the steady state on the middle, unstable branch P_1P_2 and X jumps to the only possible stable branch for $B > B_1$, namely P_2P_3. A similar reasoning shows that X undergoes a downward transition $P_2 \rightarrow P_2'$ at a smaller B, B_2, when B is decreased from some large value.

4. STEADY STATE SOLUTION OF THE MASTER EQUATION

Although the gross features of the phase transition are indicated by the preceding "deterministic" mean value analysis, which completely ignored fluctuations, considerably more information is contained in the number probability function $P(x, t)$ satisfying the master equation (3). It can be shown that a stationary solution $P^s(x)$ of Eq. (3) is unique, stable, and time independent.(14) Thus, on setting $\partial P^s(x)/\partial t = 0$ in Eq. (3), we obtain the following set of difference equations:

$$\begin{array}{llll} \vdots & \vdots & \vdots & \\ t_+(x-1)P^s(x-1) & +\, t_-(x+1)P^s(x+1) & -\, [t_-(x) + t_+(x)]P^s(x) & = 0 \\ \vdots & \vdots & \vdots & \\ t_+(0)P^s(0) & +\, t_-(2)P^s(2) & -\, [t_-(1) + t_+(1)]P^s(1) & = 0 \\ & t_-(1)P^s(1) & -\, t_+(0)P^s(0) & = 0 \end{array} \tag{9}$$

where we have denoted

$$t_+(x) = k_1 A x(x-1) + k_3 A, \qquad t_-(x) = k_2 x(x-1)(x-2) + k_4 x \tag{10}$$

The solution of the set of equations (9) is

$$P^s(x) = P^s(0) \prod_{i=1}^{x} \frac{t_+(i-1)}{t_-(i)} \tag{11}$$

The system possesses the property of detailed balance in the stationary state, as can be seen from Eq. (11), which implies

$$t_-(x+1) P^s(x+1) = t_+(x) P^s(x) \tag{12}$$

This is a general property of systems for which only transitions between neighboring states in a one-dimensional array are allowed with vanishing transitions at the boundaries of the configuration space.(15)

Alternatively, this solution may be expressed in terms of the stationary potential $\phi^s(x)$(15) defined by

$$P^s(x) = P^s(0) \exp[-\phi^s(x)] \tag{13}$$

where

$$\phi^s(x) = \sum_{i=1}^{x} \ln \left(\frac{t_-(i)}{t_+(i-1)} \right) \tag{14}$$

An asymptotic form for $\phi^s(x)$ and hence $P^s(x)$ can be obtained from Eq. (13) by replacing the sum by an integral. Application of the Euler–Maclaurin summation formula yields

$$\begin{aligned} \phi^s(x) \approx{} & (x-1) \ln\{(x+1)[x(x-1)+R]/Be[x(x-1)+P]\} \\ & - \ln B + \frac{1}{2} \ln(x+1) \\ & + 2\sqrt{R} \arctan(\sqrt{R}/x) - 2\sqrt{P} \arctan(\sqrt{P}/x) \end{aligned} \tag{15}$$

A similar form may be obtained from Eq. (11) by factoring the terms inside the product sign into gamma functions and using Stirling's approximation. A similar model of a chemical reaction has been analyzed using entirely different methods (Hamilton–Jacobi techniques) by Kitahara,(16) who obtained an equivalent result to Eq. (15).

The turning points of the stationary distribution may be deduced by noting that $P(x) = P(x-1)$ at the turning points, which together with the detailed balance condition (12) yields

$$B(x) = x[(x-1)(x-2) + R][(x-1)(x-2) + P]^{-1} \tag{16}$$

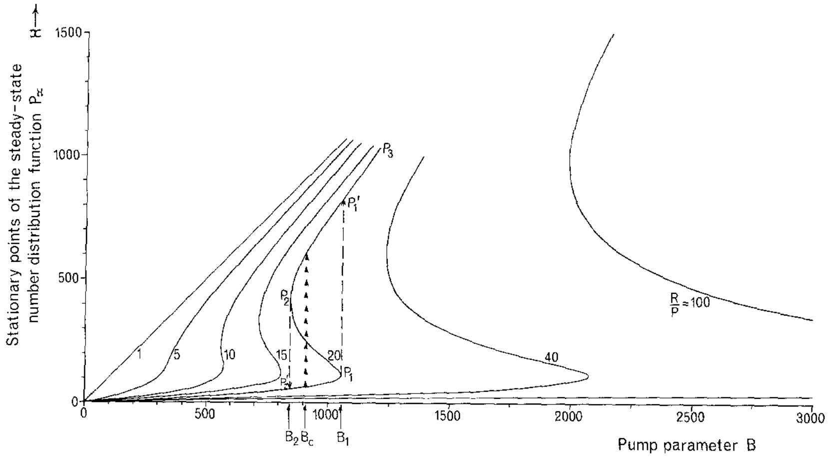

Fig. 1. The turning points of the steady state stochastic probability distribution (identical with the macroscopic mean number X) are plotted against the pump parameter B for various values of R/P and $P = 10^4$. Here – – – denotes the stochastic mean values of the steady state probability distribution.

The function $x = x(B)$ found by inverting Eq. (16) gives the turning point values corresponding to that value of B for a given P and R and can be shown to be either single-valued for all B if $R \leqslant 9P$ or triple-valued over some closed interval of B if $R > 9P$. The turning points of the steady state distribution are plotted in Fig. 1. These lie along precisely (for large X) the same curve as the steady state mean values obtained from the deterministic equation (5).

Numerical calculation of $\langle x\rangle$, the mean of the steady state distribution $P^s(x)$ defined by Eq. (11), is also shown in Fig. 1. The interesting feature is the very small range of B over which $\langle x\rangle$ shows a rapid increase. A typical variation of $P^s(x)$ with pump parameter B in the region of this transition is shown in Fig. 2. Corresponding to the almost discontinuous jump in $\langle x\rangle$ with increasing B, the strong peak of $P^s(x)$ shifts rapidly from the lower to upper branch. Some interesting features of this transition can be seen from the equation

$$B(\partial/\partial B)\langle x^k\rangle = \langle x^{k+1}\rangle - \langle x\rangle\langle x^k\rangle \tag{17}$$

relating the steady state moments of the distribution (11). For $k = 1$ we see that the variance of the distribution is directly proportional to the slope of the $\langle x\rangle$ vs. B curve

$$\sigma^2 = B\,\partial\langle x\rangle/\partial B \tag{18}$$

Below the transition point B_c (see Fig. 1) the system is on the lower branch, which is asymptotic in the limit of small x to the line $B = Rx/P$. This is the

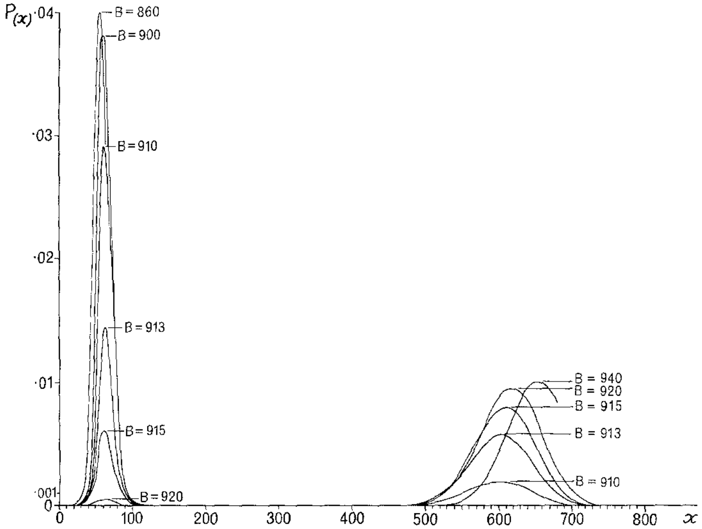

Fig. 2. Steady state probability distributions for various values of the pump parameter B near the critical point.

modal value curve for the steady state distribution for the reaction (2) alone. This steady state distribution is Poissonian with mean and variance BP/R. Similarly, the upper branch is asymptotic to the line $B = x$, the modal curve for the reaction (1) alone. The steady state distribution is Poissonian with mean and variance B.

As the pump parameter B is increased from zero, the stationary distribution corresponds closely to the Poisson distribution in number space associated with the linear reaction (2) dominating and inhibiting the nonlinear reaction (1). When the critical value B_c is reached the system switches abruptly to the upper branch and the nonlinear reaction mechanism dominates. Equation (17) shows that there are large fluctuations in x at this transition point. It may be seen that this change in $\langle x\rangle$ approaches a discontinuity with increasing system size. An analogy can be drawn with a liquid–gas system by making the correspondence $\langle x\rangle \leftrightarrow \rho$ (density) and $B \leftrightarrow P$ (pressure), and increasing the rate constant R/P corresponds to increasing temperature the T. This singularity in the response function $\partial\langle x\rangle^{-1}/\partial B$ corresponds to a singularity in the isothermal compressibility.(17)

The stationary behavior of the stochastic mean does not of course exhibit a hysteresis (see Fig. 1). This was the result obtained by Turner,(18) who incorrectly deduced from this that the stochastic analysis predicted an absence of hysteresis.

Although $\langle x\rangle$ is very close to one or other of the modal values of $P^s\langle x\rangle$ (except in the vicinity of B_c), $P^s(x)$ is nevertheless bimodal over the

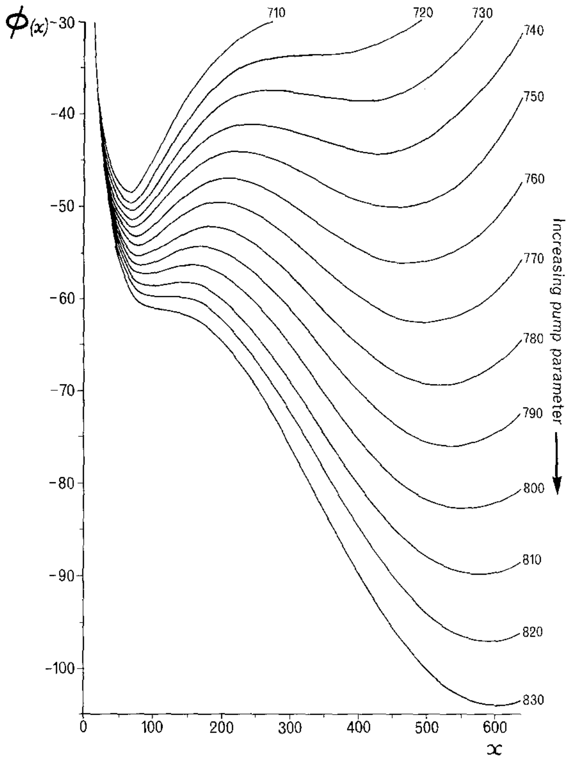

Fig. 3. The potential function $\phi^s(x)$ in the bimodal probability function region shown for various values of the pump parameter B.

entire interval in which $x(B)$ is triple-valued, as can be seen from Fig. 3, which shows the potential surface $\phi^s(x, B)$ defined by Eq. (13) for $R = 1.5 \times 10^5$, $P = 10^4$, and B ranging from 710 to 830.

This bimodal distribution must be interpreted as follows: The mean time spent by the system in any number state x is $[t_+(x) + t_-(x)]^{-1}$, as inspection of Eq. (3) will show. This does not vary appreciably over the bimodal range of $P^s(x)$. Hence in order to generate a long-time average probability distribution like that of Fig. 2, the system must spend most of its time fluctuating around either one of the two maxima, with infrequent transitions from one mode to the other as a result of sufficiently large fluctuations in the direction of the other state.

An estimate of the frequency of these transitions is made in the next section.

Clearly, if the minimum probability between the two maxima is comparatively small, transitions between states will be quite infrequent. Then the fluctuations around the means are on a much shorter time scale than the fluctuations between states.

We see now how a hysteresis in the $\langle x \rangle$, B plane may arise from this stochastic description. In the bimodal region both states are stable with respect to fluctuations below a certain critical size, defined by the distance of the respective maxima from the minimum of $P^s(x)$. A fluctuation greater than this size will drive the system into the other state. If the pump parameter is continuously increased from zero along the line OP_1 of Fig. 1, the system will remain on the lower branch (in the mean), until nearly P_1, where the transition rate from the lower state will have become of the same order as the time spent in this metastable state. This transition rate increases because the critical size of the upward fluctuation needed is decreasing. Thus the degree of hysteresis that is likely to be observed depends on how much smaller the time scale over which the pump parameter is increased is than that of transitions between bistable states. In terms of the stationary potential function $\phi^s(x)$ this is clearly seen in Fig. 3, where B is stepped completely through the bimodal range.

5. TIME-DEPENDENT BEHAVIOR

We return again to the master equation (3), which can be written as a matrix equation

$$\partial \mathbf{P}/\partial t = M\mathbf{P} \tag{19}$$

where $\mathbf{P}$ is a column vector containing all the $P(x, t)$ and M is the transition matrix. By seeking solutions of the form

$$P(x, t) = \sum_{p=0}^{\infty} P^{(p)} e^{-\lambda(p)t} \tag{20}$$

the solution of Eq. (19) becomes an eigenvalue problem, the solution of which by numerical methods is in progress. Here we will seek a continuous solution to the master equation by replacing it by a continuum differential form. Expanding $P(x - 1, t)$ and $P(x + 1, t)$ about $P(x, t)$, Eq. (3) becomes

$$\begin{aligned} \frac{\partial}{\partial t} P(x, t) &= [t_-(x + 1) - t_-(x) - t_+(x) + t_+(x - 1)]P(x, t) \\ &\quad + [t_-(x + 1) - t_+(x - 1)] \frac{\partial P(x, t)}{\partial x} \\ &\quad + \frac{1}{2}[t_-(x + 1) + t_+(x - 1)] \frac{\partial^2 P(x, t)}{\partial^2 x^2} \end{aligned} \tag{21}$$

where Eq. (21) has been truncated above second-order derivatives. It is then basically on a Fokker–Planck equation for a Markov process in the continuous variable x with nonlinear drift and diffusion coefficients.

Physically this procedure can be justified by scaling x to be independent of the system size. Then the coefficients of derivatives of subsequent orders in the expansion (21) of the master equation decrease in order of magnitude by a factor increasing with the size of the system,(19) provided the fluctuations have their origin in microscopic noncollective effects.(15) In this system the fluctuations involving transitions between alternative states are in fact of this nature and the truncated expansion (21) is really only valid for fluctuations around one of the local probability maxima.(20,21) Nevertheless, by making this approximation we preserve the general bistable feature of the system without the severe analytic complexity of the full expansion. In any case, comparison can be made with the steady state solution obtained with that obtained exactly from the master equation.

Equation (21) is not quite in the usual Fokker–Planck form. However, if we assume that $x \gg 1$, we can approximate Eq. (21) very well by

$$\frac{\partial}{\partial t} P(x, t) = -\frac{\partial}{\partial x}\{\langle \dot{x} \rangle P(x, t)\} + \frac{\partial^2}{\partial x^2}\{D(x)P(x, t)\} \tag{22}$$

where

$$D(x) = \tfrac{1}{2}\{t_+(x-1) + t_-(x)\}, \qquad \langle \dot{x} \rangle = t_+(x-1) - t_-(x) \tag{23}$$

The second term in Eq. (22) represents the diffusive effects of fluctuations about the macroscopic behavior. Defining a probability flux or ensemble density flow in configuration space by the one-dimensional continuity equation

$$\frac{\partial P}{\partial t} + \frac{\partial j}{\partial x} = 0 \tag{24}$$

Eq. (22) can be integrated to give

$$j(x, t) = P(x, t)\langle \dot{x} \rangle - (\partial/\partial x)\{D(x)P(x, t)\} \tag{25}$$

In the steady state $j(x, t) = 0$, and Eq. (25) yields for the derivative of the stationary potential function

$$\frac{\partial \phi^s(x)}{\partial x} = 2\,\frac{t_-(x) - t_+(x+1)}{t_+(x-1) + t_-(x)} \tag{26}$$

since $\partial D(x)/\partial x \ll D(x)$ for $x \gg 1$.

To investigate the accuracy of this solution, we recall that we have an excellent continuum form for $\phi^s(x)$ [Eq. (15)] obtained from the exact solution of the master equation. This yields on differentiation

$$\partial \phi^s(x)/\partial x = \ln\{t_-(x+1)/t_+(x)\} \tag{27}$$

which can be expanded as

$$\frac{\partial\phi^s(x)}{\partial x} = 2\left\{\frac{t_-(x+1) - t_+(x)}{t_+(x+1) + t_-(x)} + \frac{1}{3}\left[\frac{t_-(x+1) - t_+(x)}{t_+(x+1) + t_-(x)}\right]^3 + \cdots\right\} \tag{28}$$

We see that the approximate solution (26) is the first term of this series. This approximation is generally sufficient provided the drift velocity $t_-(x) - t_+(x)$ is not too large. Near the stationary points of the distribution, $\partial\phi^s(x)/\partial x \approx 0$ and the agreement is very good indeed.(22)

We can use this analysis to obtain an estimate of the lifetimes of the metastable states and hence of the time scale of the fluctuations between states by adopting a method originally given by Kramers(23) and subsequently developed by various authors.(24–26)

We find that the ratio of the time scale of the fluctuations between the metastable states τ and the local fluctuations within one of the probability maxima τ_{x_2} is given by

$$\tau/\tau_{x_2} = 2\pi(e^{-\Delta(+)} + e^{-\Delta(-)})^{-1} \tag{29}$$

where the activation potentials $\Delta^{(\pm)}$ are the heights of the potential barrier of Fig. 3 above the two minima.[3] In the thermodynamic limit this ratio becomes infinite and we approach the deterministic result of two essentially stable steady states. The derivation of Eq. (29) is given in the appendix.

This result is similar to that obtained by Landauer(26) for tunnel diodes by a slightly different but equivalent method. The similarity with the familiar problem of a thermally activated jump across a potential barrier is obvious. This approach has been useful in estimating the minimum useful size of Esaki diodes as bistable computing devices.(27) This limit is set by the criterion that the critical fluctuation size needed to change the diode state is much greater than the magnitude of the thermal fluctuations.

6. CONCLUSION

A stochastic analysis of a first-order phase transition in a model chemical reaction has been given using a simple birth–death Markovian type master equation. The steady state probability distribution $P^s(x)$ is found to be bimodal in the region of the transition from one stable branch to the other. It is shown that this microscopic analysis predicts a hysteresis of a similar nature to that predicted by a macroscopic analysis. An approximate solution to the time-dependent master equation in the continuum limit yields an estimate of the time scale over which a transition from one metastable steady state to the other takes place. This is shown to vary as $e^{\Delta\phi}$, where $\Delta\phi$ is the

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[3] It has been brought to our attention that a similar result has been obtained by Janssen using a different method.(29)

height of a generalized thermodynamic potential barrier between the two states. In the thermodynamic limit this time scale tends to infinity and we have essentially two alternative stable steady states, in agreement with the macroscopic results.(9)

The model chosen for the chemical reaction assumes an essentially infinite coherence length. That is, no account is taken of spatial effects, such as diffusion. A promising approach to include diffusion in stochastic models of chemical reactions has recently been advanced.(16,28) Work is at present proceeding to include diffusion effects into our present model.

APPENDIX. DERIVATION OF EQ. (29)[4]

The derivation of Eq. (29) is based on the assumption that the equilibration process within each well of the potential $\phi^s(x)$ is fast compared to the processes that require motion through the unlikely state at x_2. Thus we write

$$P(x, t) = \beta(x, t)P^s(x) \tag{A.1}$$

where $\beta(x)$ is essentially constant within each well and changes only in the vicinity of x_2. As time progresses, $\beta(x)$ relaxes toward unity.

For a current j in the vicinity of x_2 we have

$$j = -D(x_2)\, \partial P(x)/\partial x \tag{A.2}$$

since $D(x)$ is slowly varying. On combining Eq. (A.1) and (A.2), we can write

$$\beta = \int \frac{-j}{D(x_2)P(x)}\, dx = \int \frac{-j}{D(x_2)P^s(0)} \exp[\phi^s(x)]\, dx \tag{A.3}$$

Since $\phi^s(x)$ is peaked around x_2, we can use a saddlepoint type of approximation to obtain

$$\beta(x_3) - \beta(x_1) = \frac{-j}{D(x_2)P(x_2)} \left[\frac{-2\pi}{\phi''(x_2)}\right]^{1/2} \tag{A.4}$$

The term $-\phi''(x)$ can be written in two ways. From the exact steady state solution to the master equation (21) one has

$$-\phi''(x_2) = (1/x_2) + O(1/x_2^2) \tag{A.5}$$

in the vicinity of x_2, whereas Eq. (26) yields

$$-\phi''(+x_2) = D(x_2)^{-1} \left.\frac{\partial\langle\dot{x}\rangle}{\partial x}\right|_{x=x_2} \tag{A.6}$$

If we write

$$v(x_2) = \frac{x - x_2}{\tau_{x_2}} \approx (x - x_2) \left.\frac{\partial\langle\dot{x}\rangle}{\partial x}\right|_{x=x_2} \tag{A.7}$$

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[4] We wish to thank Dr. R. Landauer for helpful correspondence on the material in the Appendix.

to describe the (macroscopic) velocity developed as we move away from the exact point of instability, Eq. (A.6) becomes

$$-\phi''(x_2) \approx \{D(x_2)\tau_{x_2}\}^{-1} \tag{A.8}$$

Clearly, $\tau_{x_2} \sim D(x_2)^{-1} = 2[t_+(x_2 - 1) + t_-(x_2)]^{-1}$, which is of the order of the inverse of the time spent by the system in any particular number state near x_2. Using, however, the expression for $\phi''(x)$ given by Eq. (A.5) in Eq. (A.4), we obtain

$$\beta(x_3) - \beta(x_1) = -j[D(x_2)P^s(x_2)]^{-1}(2\pi x_2)^{1/2} \tag{A.9}$$

Now we have seen that the stationary distribution peaks are very nearly of Poisson shape [see Eq. (17)] whose total probability population $N(x_i)$ is related to the modal value by

$$N(x_i) = (2\pi x_i)^{1/2}P(x_i) \tag{A.10}$$

Since we have put $P(x, t) = \beta(x, t)P^s(x)$, the integrated ensemble populations near the maxima at x_1 and x_3 are given by

$$\begin{aligned} N(x_1) &= P^s(x_1)\beta(x_1)(2\pi x_1)^{1/2} \\ N(x_3) &= P^s(x_3)\beta(x_3)(2\pi x_3)^{1/2} \end{aligned} \tag{A.11}$$

Defining "activation potentials" $\Delta^{(-)}$ and $\Delta^{(+)}$ by

$$e^{\Delta(-)} = N^s(x_2)/N^s(x_2), \qquad e^{\Delta(+)} = N^s(x_3)/N^s(x_2) \tag{A.12}$$

where $N^s(x_2)$ is a fictitious population defined in formal analogy with Eq. (A.10) as

$$N^s(x_2) = P^s(x_2)(2\pi x_2)^{1/2} \tag{A.13}$$

$N^s(x_2)$ is a measure of the exponential inaccessibility of x_2 in the region over which β varies appreciably. The activation potentials Δ are the heights of the potential barrier of Fig. 3 above the two minima. In terms of these definitions, Eqs. (A.9) and (A.11) become

$$\beta(x_3) - \beta(x_1) = -j(2\pi x_2)/N^s(x_2)D(x_2) \tag{A.14}$$

$$N(x_2) = \beta(x_1)e^{\Delta(-)}N^s(x_2) \tag{A.15}$$

$$N(x_3) = \beta(x_3)e^{\Delta(+)}N^s(x_2) \tag{A.16}$$

Clearly

$$j = -\partial N(x_1)/\partial t = \partial N(x_3)/\partial t \tag{A.17}$$

which combined with Eqs. (A.14)–(A.16) yields the two coupled first-order differential equations

$$-j = D(x_2)[N(x_3)e^{-\Delta(-)} - N(x_1)e^{-\Delta(+)}](2\pi x_2)^{-1} = \dot{N}(x_1) = -\dot{N}(x_3) \tag{A.18}$$

the solutions of which are

$$N(x_2) = N^s(x_1)(1 - e^{-t/\tau}) - N_{\mathrm{initial}}(x_1)e^{-t/\tau} \tag{A.19}$$

$$N(x_3) = N^s(x_3)(1 - e^{-t/\tau}) - N_{\mathrm{initial}}(x_3)e^{-t/\tau} \tag{A.20}$$

where $\tau^{-1} = D(x_2)(e^{-\Delta(-)} + e^{-\Delta(+)})(2\pi x_2)^{-1}$,

which in view of Eq. (A.8) can be written

$$\tau^{-1} = (2\pi\tau_{x_2})^{-1}(e^{-\Delta(-)} + e^{-\Delta(+)}) \tag{A.21}$$

which is the result (29).

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