# Critical behavior of a class of nonlinear stochastic models with cubic interactions

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A theoretical analysis based on the method of system-size expansion of the master equation is carried out for a generalized nonlinear stochastic model with cubic interactions. The resulting Fokker-Planck equation enables us to derive the relevant probability distributions in the critical region as well as away from it; in the former case, the distribution turns out to be non-Gaussian and is dominated by fluctuations which are non-negligible. The onset of a first-order phase transition in the system is investigated in some detail. In particular, a Maxwell-type "theorem of equal areas" is discovered which might hold for a much wider class of systems with cubic interactions.

## I. INTRODUCTION

The phenomena of phase transitions in open physical systems have been extensively investigated during the last two decades.[1–10] The major ingredients in these investigations have been the role played by nonlinearity in the underlying structure of the problem in bringing about the phenomena in question and the recognition that, when the macroscopic state of such a system is driven beyond a critical distance from the state of transient equilibrium, initially microscopic fluctuations and random forces may give rise to the onset of instabilities which in turn lead to the emergence of a new state of macroscopic order. Such an instability may be symmetry breaking, in which case, beyond a critical affinity, the response of the system to an infinitesimal disturbance leads ultimately to a new operating regime characterized by temporal or spatial organization. For instabilities which are not symmetry breaking, the macroscopic kinetic equations involve a nonlinearity of at least cubic order and predict a region of overall affinity and/or influence in which a trio of homogeneous steady states become accessible to the system.[5–8,11–13] In the latter case, the middle branch of the resulting $S$-shaped steady-state curve is infinitesimally unstable, while the lower and upper branches remain stable throughout the region of coexistence.

A common meeting ground for macroscopic models with multiple steady states, ranging from the ones in physics,[14,15] chemical kinetics,[5–8,12,13] and biochemistry[16–20] to those in population dynamics,[21] ecology,[22] and sociology,[23] is that they all deal with populations involving a large number of units interacting nonlinearly. An important question in this regard is as to when a general, real system with accessibility to multiple steady states will actually jump from one stable branch to another. As the relevant parameter of the problem is increased, will the system remain on the lower branch until it reaches the extreme point of infinitesimal instability $B_1$ (see Fig. 1) or will it be driven to the upper branch at some earlier point, for example, $B_c$? For the vapor-liquid phase transition of a van der Waals gas, the well-known Maxwell construction of equal areas, which is based on the equality of chemical potentials of the two phases in coexistence, provides the desired answer. For a general system, however, this question is still largely unanswered. In the present investigation we have approached this problem from a stochastic point of view and have shown that a rigorous criterion based on the division of probabilities does ultimately lead to the conclusion that, in the zeroth approximation, the transition from one stable branch to another takes place when the response curve of the problem carves out equal areas with the deterministic $S$-shaped curve, i.e., a sort of "theorem of equal areas" is indeed obeyed.

In a recent paper we have analyzed the critical behavior of a class of nonlinear stochastic models of diffusion of information with quadratic birth and death rate constants[24] and have shown that, in spite of the fundamental differences in the structure and conception of open and closed systems, they display identical mathematical behavior in their critical regions. In other words, open and closed systems may be regarded as locally isomorphic at their critical points, with the result that the relevant features emerging from the nonlinearity of the problem

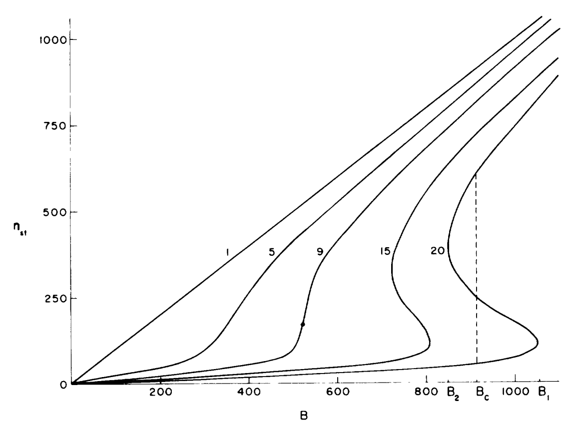


FIG. 1. Steady-state solutions of the macroscopic equation (48) vs the pump parameter $B$, with $P=10^4$ and $R/P=1$, 5, 9, 15, and 20. Critical point is shown for $R/P=9$ and the turning points $B_1$ and $B_2$ are shown for $R/P=20$.

 

are independent of the underlying structures of the systems in question and, in their critical regions, are model invariant. Our analysis dispelled the notion that the birth-and-death type of a model is in itself inadequate to give a complete description of critical fluctuations in a nonequilibrium system. In fact, a modified version of van Kampen's method[25,26] of system-size expansion of the master equation, as recently developed by Fox[27] (while elucidating the relationship between Keizer's theory of nonequilibrium thermodynamics and the master equation approach) and by Dekker[28] (in connection with a study of the Malthus-Verhulst process with spontaneous generation), was successfully applied to the birth-and-death type of stochastic models for examining the statistical behavior of both equilibrium and nonequilibrium systems in their critical regions. In this paper we propose to extend that study to systems with cubic interactions. Though our analysis is intended to apply to a general nonlinear system with cubic interactions, we find it convenient to couch it in the language of our previous paper which addressed itself to the problem of diffusion of information in a homogeneously mixing population.

## II. MODEL

To begin with, we observe that, for the occurrence of a first-order phase transition in the given system interactive processes must generate nonlinearities which are at least cubic in nature. In view of this we consider a model in which the growth and decay of the variable of interest, $n(t)$, is governed by birth and death rate constants, $\lambda_n$ and $\mu_n$, which are cubic in $n$; this will encompass several models encountered in chemical kinetics and in physical, biological, and sociological problems as special cases. In the context of diffusion of information, $n(t)$ will denote the number of active spreaders of information at time $t$. Thus, we write

$$\lambda_n = a + bn + c\Omega^{-1}n^2 + e\Omega^{-2}n^3 \tag{1}$$

and

$$\mu_n = a' + b'n + c'\Omega^{-1}n^2 + e'\Omega^{-2}n^3 , \tag{2}$$

where $\Omega$ is a measure of the overall size of the system. We may add that, in order to avoid the eventual "extinction" or "blowing up" of the process, we must have

$$a > a' \quad \text{and} \quad e < e' . \tag{3}$$

The precise genesis of the rates (1) and (2) depends on the actual problem at hand; a detailed example will be discussed in Sec. V.

Introducing the translation operator $E$, defined by

$$E^{\pm 1} f(n) = f(n \pm 1) , \tag{4}$$

the master equation of the (one-step) process can be written in the form

$$\dot{p}(n,t) = [(E^{-1}-1)\lambda_n + (E-1)\mu_n]p(n,t) . \tag{5}$$

In the spirit of the system-size expansion technique, we split the random variable $n(t)$ into a deterministic component and a stochastic component,

$$n(t) = \Omega\phi(t) + \Omega^{\nu}x(t), \quad 0 < \nu < 1 \tag{6}$$

such that the stochastic variable $x(t) = O(1)$. The probability distribution $p(n,t)$ now transforms into $\Pi(x,t)$, where

$$\Pi(x,t) = \Omega^{\nu} p[\Omega\phi(t) + \Omega^{\nu}x, t] , \tag{7}$$

while

$$(E^{\pm 1} - 1) = \pm\Omega^{-\nu}\frac{\partial}{\partial x} + \frac{\Omega^{-2\nu}}{2}\frac{\partial^2}{\partial x^2} \pm \cdots . \tag{8}$$

Substituting (6)–(8) into (5) and using (1) and (2), we obtain

$$\frac{\partial \Pi}{\partial t} - \Omega^{1-\nu}\frac{d\phi}{dt}\frac{\partial \Pi}{\partial x} = -\Omega^{1-\nu}\frac{\partial}{\partial x}[\alpha_1(\phi,x)\Pi] + \tfrac{1}{2}\Omega^{1-2\nu}\frac{\partial^2}{\partial x^2}[\alpha_2(\phi,x)\Pi] + \cdots , \tag{9}$$

where

$$\alpha_1(\phi,x) = (a-a')\Omega^{-1} + (b-b')(\phi + \Omega^{\nu-1}x) + (c-c')(\phi+\Omega^{\nu-1}x)^2 + (e-e')(\phi+\Omega^{\nu-1}x)^3 \tag{10}$$

and

$$\alpha_2(\phi,x) = (a+a')\Omega^{-1} + (b+b')(\phi + \Omega^{\nu-1}x) + (c+c')(\phi+\Omega^{\nu-1}x)^2 + (e+e')(\phi+\Omega^{\nu-1}x)^3 . \tag{11}$$

The leading terms in (9) are of order $\Omega^{1-\nu}$ and lead to the deterministic equation

$$\frac{d\phi}{dt} = (b-b')\phi + (c-c')\phi^2 + (e-e')\phi^3 , \tag{12}$$

with the assumption that the term $(a-a')\Omega^{-1}$ does not contribute to this order. Terms of the next order lead to the Fokker-Planck equation

$$\frac{\partial \Pi}{\partial t} = -\frac{\partial}{\partial x}[f(\phi,x)\Pi] + \frac{1}{2}\frac{\partial^2}{\partial x^2}[g(\phi,x)\Pi] + \cdots , \tag{13}$$

where

$$f(\phi,x) = (a-a')\Omega^{-\nu} + [(b-b') + 2(c-c')\phi + 3(e-e')\phi^2]x + [(c-c') + 3(e-e')\phi]x^2\Omega^{\nu-1} + (e-e')x^3\Omega^{2\nu-2}$$

and

$$g(\phi,x)=(a+a')\Omega^{-2\nu}+[(b+b')\phi+(c+c')\phi^2+(e+e')\phi^3]\Omega^{1-2\nu}+[(b+b')+2(c+c')\phi+3(e+e')\phi^2]x\Omega^{-\nu}+[(c+c')+3(e+e')\phi]x^2\Omega^{-1}+(e+e')x^3\Omega^{\nu-2} .$$

Far away from the critical region, the conventional scheme of van Kampen, with $\nu=\frac{1}{2}$, applies. In the critical region the scaling index $\nu$ depends upon the detailed nature of the functions $\alpha_1(\phi,x)$ and $\alpha_2(\phi,x)$. Before immersing ourselves in the investigation of this particular question it seems advisable to first examine the macroscopic or phenomenological evolution of the process.

## III. MACROSCOPIC EVOLUTION OF THE PROCESS

For this we examine the deterministic Eq. (12) whose solution, with the initial condition $\phi(0)=\phi_0$, is given by the implicit relationship

$$\left[\frac{\phi-\phi_1}{\phi_0-\phi_1}\right]^{\phi_3-\phi_2}\left[\frac{\phi-\phi_2}{\phi_0-\phi_2}\right]^{\phi_1-\phi_3}\left[\frac{\phi-\phi_3}{\phi_0-\phi_3}\right]^{\phi_2-\phi_1}=\exp[(e-e')(\phi_1-\phi_2)(\phi_2-\phi_3)(\phi_3-\phi_1)t] , \quad (14)$$

where $\phi_1\le\phi_2\le\phi_3$ are the steady-state solutions of (12):

$$\phi_1=0 ,$$

$$\phi_{2,3}=\frac{1}{2(e'-e)}\{(c-c')\pm[(c-c')^2-4(e-e')(b-b')]^{1/2}\} .$$

Since $e<e'$ it follows from (14) that, as $t\to\infty$, $\phi\to\phi_1$, $\phi_2$, or $\phi_3$ accordingly as $\phi_0$ is less than, equal to, or greater than $\phi_2$.

We observe that the steady-state solutions $\phi_{st}$ of (12) represent two-parameter families of curves in the $bc$ plane, the point $(b',c')$ being the critical point of the system. Of course, $\phi_{st}$ must be non-negative and, for linear stability,[4,29] we must have

$$\Delta=[(b-b')+2(c-c')\phi_{st}+3(e-e')\phi_{st}^2]<0 . \quad (15)$$

Regarding $b'$ and $c'$ as fixed, and $b$ and $c$ as variable, the stable solutions then are as follows.

(i) For $\{(b-b')\le 0, (c-c')<[4(e-e')(b-b')]^{1/2}\}$,

$$\phi_{st}=0 . \quad (16)$$

(ii) For $\{(b-b')\le 0, (c-c')\ge[4(e-e')(b-b')]^{1/2}\}$ and for $[(b-b')>0, c\ge 0]$,

$$\phi_{st}=\frac{1}{2(e'-e)}\{(c-c')+[(c-c')^2-4(e-e')(b-b')]^{1/2}\} . \quad (17)$$

For $c-c'=[4(e-e')(b-b')]^{1/2}$, we have

$$\phi_{st}=\frac{(c-c')}{2(e'-e)}=\left[\frac{|b-b'|}{e'-e}\right]^{1/2} . \quad (18)$$

Moreover, along $b=b'$ and $c>c'$,

$$\phi_{st}=\frac{(c-c')}{(e'-e)} , \quad (19)$$

while along $c=c'$ and $b>b'$,

$$\phi_{st}=\left[\frac{b-b'}{e'-e}\right]^{1/2} . \quad (20)$$

## IV. SCALING INDICES AND THE CRITICAL REGION

The study of the situation in the close vicinity of the critical point ($b\simeq b'$, $c\simeq c'$) needs some special care. First of all we recall that, while writing Eq. (12), we have already assumed that $(a-a')$ is at best $o(\Omega)$; now it can be seen that the limiting forms, $\tilde{\alpha}_1(\phi)$ and $\tilde{\alpha}_2(\phi)$, of the first and second jump moments $\alpha_1(\phi,x)$ and $\alpha_2(\phi,x)$, as $\Omega\to\infty$, possess several vanishing derivatives in the steady state at the critical point ($b=b'$, $c=c'$). Suppose that the first nonvanishing derivatives of $\tilde{\alpha}_1(\phi)$ and $\tilde{\alpha}_2(\phi)$ at $\phi=\phi_{st}$ are of order $q$ and $p$, respectively; then the drift and diffusion coefficients $f(\phi,x)$ and $g(\phi,x)$ in the Fokker-Planck equation (13) turn out to be of order $\Omega^{(\nu-1)(q-1)}x^q$ and $\Omega^{(\nu-1)(p-1)-\nu}x^p$, respectively. Since the variable $x$ is supposed to be $O(1)$, we must have

$$\nu=\frac{q-p}{q-p+1} . \quad (21)$$

At the same time, the critical slowing down index $\mu$, which implies that the approach towards the steady state is slowed down by a factor of order $\Omega^{\mu}$, is given by

$$\mu=\frac{q-1}{q-p+1} . \quad (22)$$

Far away from the critical region we have the standard situation, viz., $q=1$ and $p=0$, with the result that $\nu=\frac{1}{2}$ and $\mu=0$. With quadratic interactions we found that in the critical region $q=2$ and $p=1$, with the result that $\nu$ was still $\frac{1}{2}$ but $\mu$ became $\frac{1}{2}$ as well. In the present case we find that if $a=a'=O(1)$ then $q=3$ and $p=1$; accordingly, both $\nu$ and $\mu$ turn out to be $\frac{2}{3}$. However, if $a,a'=O(\Omega)$ such that $(a-a')=o(\Omega)$, we then find the following instead: $q=3$ and $p=0$, whence $\nu=\frac{3}{4}$ and $\mu=\frac{1}{2}$. In both these cases, the situation in the close neighborhood of the critical point will be very different from the one encountered far away from the critical point. To have an inkling of this, let us look at the equation of motion of the first moment, which can be readily obtained by substituting the rate constants (1) and (2) into the master equation (5), multiplying throughout by $n$, and summing over all values of $n$; we thus obtain

$$\frac{d}{dt}\langle n\rangle=\langle(a-a')+(b-b')n+(c-c')\Omega^{-1}n^2+(e-e')\Omega^{-2}n^3\rangle . \quad (23)$$

It follows that in the steady state of the system, and at the critical point ($b=b'$, $c=c'$),

$$\langle n^3\rangle_{\rm st,cr}=\left[\frac{a-a'}{e'-e}\right]\Omega^2=O(\Omega^2) \tag{24}$$

and hence

$$\langle n\rangle_{\rm st,cr}=O(\Omega^{2/3}) . \tag{25}$$

It is then natural to define the critical region in the $bc$ plane as one in which $\langle n\rangle_{\rm st}=O(\Omega^{2/3})$. Equations (16)–(20) and (23) then tell us that in this region

$$|b-b'|=O(\Omega^{-2/3}),\quad |c-c'|=O(\Omega^{-1/3}) , \tag{26}$$

with $\phi_{\rm st}=O(\Omega^{-1/3})$. In the other case, we have instead

$$|b-b'|=O(\Omega^{-1/2}),\quad |c-c'|=O(\Omega^{-1/4}) , \tag{27}$$

with $\phi_{\rm st}=O(\Omega^{-1/4})$. It is important to observe that in each case, in the critical region defined as above, the two parts of the random variable $n(t)$, viz., the deterministic part $\Omega\phi_{\rm st}$ and the stochastic part $\Omega^{\nu}x(t)$, turn out to be of the same order of magnitude.

We shall now examine the probability distribution $\Pi(x,t)$ for these two cases.

### A. Case I ($\nu=\frac{2}{3}$)

Setting

$$b-b'=\eta_1 b'\Omega^{-2/3},\quad c-c'=\eta_2 b'\Omega^{-1/3} ,$$
$$e'-e=b'\xi>0 , \tag{28}$$

we obtain

$$\phi_{\rm st}=\Omega^{-1/3}A,\quad A=\frac{1}{2\xi}[\eta_2+(\eta_2^2+4\eta_1\xi)^{1/2}] . \tag{29}$$

The Fokker-Planck equation (13) then reduces to

$$\frac{\partial\Pi}{\partial t}=b'\Omega^{-2/3}\left[-\frac{\partial}{\partial x}\{[\omega+(\eta_1+2A\eta_2-3A^2\xi)x+(\eta_2-3A\xi)x^2-\xi x^3]\Pi\}+\frac{\partial^2}{\partial x^2}[(A+x)\Pi]\right] , \tag{30}$$

where $\omega=(a-a')/b'>0$. The common factor $\Omega^{-2/3}$ on the right-hand side of (30) signifies the phenomenon of critical slowing down mentioned above. In the steady state we obtain

$$\Pi(\eta_1,\eta_2,x)=\text{const}(A+x)^{(\omega-1)}\times\exp[-(\eta_2^2+4\eta_1\xi)^{1/2}x^2-\tfrac{1}{3}\xi x^3] . \tag{31}$$

At the critical point ($\eta_1=\eta_2=0$), $A=0$ and hence

$$\Pi_c(x)=\text{const}\,x^{\omega-1}\exp(-\tfrac{1}{3}\xi x^3) . \tag{32}$$

In terms of the variable $\rho(=n\Omega^{-1}=\phi+\Omega^{-1/3}x)$, Eq. (31) takes the very suggestive form

$$\Pi(\rho)=\text{const}\rho^{\omega-1}\exp(\eta_1\Omega^{1/3}\rho+\tfrac{1}{2}\eta_2\Omega^{2/3}\rho^2-\tfrac{1}{3}\xi\Omega\rho^3) , \tag{33}$$

which at the critical point reduces to

$$\Pi_c(\rho)=\text{const}\rho^{\omega-1}\exp(-\tfrac{1}{3}\xi\Omega\rho^3) . \tag{34}$$

The moments of the distribution (33) can be obtained in the close vicinity of the critical point by using standard forms[30] of the integrals involved; at the critical point itself

$$\bar{\rho}_c=\left[\frac{3}{\xi\Omega}\right]^{1/3}\frac{\Gamma((\omega+1)/3)}{\Gamma(\omega/3)} \tag{35}$$

and

$$[\rho_c^2]_{\rm av}=\left[\frac{3}{\xi\Omega}\right]^{2/3}\frac{\Gamma((\omega+2)/3)}{\Gamma(\omega/3)} . \tag{36}$$

Further, the rate of growth of $\bar{\rho}$ with the parameters $\eta_1$ and $\eta_2$ is given by

$$\left[\frac{\partial\bar{\rho}}{\partial\eta_1}\right]_{\omega,\eta_2,\xi}=\Omega^{1/3}([\rho^2]_{\rm av}-\bar{\rho}^2) \tag{37}$$

and

$$\left[\frac{\partial\bar{\rho}}{\partial\eta_2}\right]_{\omega,\eta_1,\xi}=\tfrac{1}{2}\Omega^{2/3}([\rho^3]_{\rm av}-\bar{\rho}[\rho^2]_{\rm av}) . \tag{38}$$

Equation (37) shows that the rate of growth of the order parameter $\bar{\rho}$ with respect to $\eta_1$ is directly proportional to the variance of $\rho$; the variation with $\eta_2$, however, is more intriguing.

### B. Case II ($\nu=\frac{3}{4}$)

When $a,a'=O(\Omega)$ such that $(a-a')=o(\Omega)$, we may then set

$$\alpha=\left[\frac{b-b'}{a'}\right]\Omega^{3/2},\quad \beta=\left[\frac{c-c'}{a'}\right]\Omega^{5/4} ,$$
$$\xi=\left[\frac{e'-e}{a'}\right]\Omega>0$$

so that

$$\phi_{\rm st}=\Omega^{-1/4}B,\quad B=\frac{1}{2\xi}[\beta+(\beta^2+4\alpha\xi)^{1/2}] .$$

Now the Fokker-Planck equation reduces to

$$\frac{\partial\Pi}{\partial t}=a'\Omega^{-3/2}\left[-\frac{\partial}{\partial x}\{[\alpha(B+x)+\beta(B+x)^2-\xi(B+x)^3]\Pi\}+\frac{\partial^2\Pi}{\partial x^2}\right] . \tag{39}$$

The common factor $a'\Omega^{-3/2}$, which is $O(\Omega^{-1/2})$, on the right-hand side of Eq. (39) determines the critical slowing down of the system. In the steady state, we obtain for $\rho = n\Omega^{-1}$

$$\Pi(\rho) = \text{const}\exp(\tfrac{1}{2}\alpha\Omega^{1/2}\rho^2 + \tfrac{1}{3}\beta\Omega^{3/4}\rho^3 - \tfrac{1}{4}\xi\Omega\rho^4) \tag{40}$$

and

$$\Pi_c(\rho) = \text{const}\exp(-\tfrac{1}{4}\xi\Omega\rho^4) \ . \tag{41}$$

At the critical point, the moments of the distribution are given by

$$\bar{\rho}_c = \left[\frac{4}{\xi\Omega}\right]^{1/4} \frac{\Gamma(\frac{1}{2})}{\Gamma(\frac{1}{4})} \tag{42}$$

and

$$[\rho_c^2]_{\text{av}} = \left[\frac{4}{\xi\Omega}\right]^{1/2} \frac{\Gamma(\frac{3}{4})}{\Gamma(\frac{1}{4})} \ . \tag{43}$$

Further, we obtain

$$\left[\frac{\partial\bar{\rho}}{\partial\alpha}\right]_{\beta,\xi} = \tfrac{1}{2}\Omega^{1/2}([\rho^3]_{\text{av}} - \bar{\rho}[\rho^2]_{\text{av}}) \tag{44}$$

and

$$\left[\frac{\partial\bar{\rho}}{\partial\beta}\right]_{\alpha,\xi} = \tfrac{1}{3}\Omega^{3/4}([\rho^4]_{\text{av}} - \bar{\rho}[\rho^3]_{\text{av}}) \ . \tag{45}$$

Equations (44) and (45) show the manner in which the rate of growth of the order parameter $\bar{\rho}$ with respect to the parameters $\alpha$ and $\beta$ is related to the higher moments of the distribution.

## V. A MODEL WITH FIRST-ORDER PHASE TRANSITION

We shall now examine certain important statistical aspects of the Matheson-Walls-Gardiner model[7] (MWG) of first-order, nonequilibrium phase transitions in chemical reactions. The formal similarity between this model and the one we have been considering for the process of diffusion of information in an open population is such that we can develop a common line of analysis appropriate for both these systems. In fact, with proper transliteration, the results of this analysis may be applied to problems in other areas as well.

By allowing three-body interactions in a homogeneously mixing population, the nonlinear reactions, as given by Eqs. (1) and (2) of MWG, describe equally well the conversion of "ignorants" into "spreaders" by two different processes: (i) through interpersonal contacts and (ii) through a mass-mediating effect. Both these processes have their inverses as well, viz., (i) a rebuff (or disenchantment) on meeting other spreaders and (ii) a spontaneous loss of interest (out of sheer boredom or whatever). The system in question is supposed to be in contact with an "infinite" reservoir $A$ comprising the general populace. With this analogy in mind, we have

$$\lambda_n = k_1 A n(n-1) + k_3 A$$

and (46)

$$\mu_n = k_2 n(n-1)(n-2) + k_4 n \ .$$

Obviously, in order that all the processes involved here are of comparable significance, we must have

$$k_3/k_1, \ k_4/k_2 = O(n^2)$$

and

$$k_1 A/k_2, \ k_3 A/k_4 = O(n) \ .$$

In the notation of our Eqs. (1) and (2),

$$a = k_3 A, \ b = -k_1 A, \ c = k_1 A\Omega, \ e \equiv 0 \ ,$$

$$a' \equiv 0, \ b' = (2k_2 + k_4), \ c' = -3k_2\Omega, \ e' = k_2\Omega^2 \ .$$

Comparing orders of magnitude, one can readily see that for a large system $b' \simeq k_4$, $b/b' \simeq 0$, and $c'/c \simeq 0$. It follows that

$$\lambda_n \mp \mu_n \simeq \mp k_2(n^3 \mp Bn^2 + Rn \mp PB) \ , \tag{47}$$

where

$$B = \frac{k_1 A}{k_2} = O(\Omega) \ ,$$

$$P = \frac{k_3}{k_1} = O(\Omega^2) \ ,$$

and

$$R = \frac{k_4}{k_2} = O(\Omega^2) \ .$$

The macroscopic rate equation, for the steady state, now reduces to

$$n^3 - Bn^2 + Rn - PB = 0 \ . \tag{48}$$

Treating $B$ as the "pump parameter," the nature of the roots of this equation depends on the ratio $R/P$. We encounter three distinct possibilities.

### A. Case (a) $R/P < 9$

In this case we have only one real root of Eq. (48) and the jump moments are such that $q = 1$ and $p = 0$, with the result that the conventional scheme of van Kampen, with $\nu = \frac{1}{2}$, applies. Accordingly, writing

$$n = \Omega\phi + \Omega^{1/2}x \ , \tag{49}$$

we obtain for the steady-state probability distribution

$$\Pi_{\text{st}}(x) \propto \exp\left[-\frac{(3\Omega^2\phi^2 - 2B\Omega\phi + R)\Omega x^2}{(\Omega^3\phi^3 + B\Omega^2\phi^2 + R\Omega\phi + PB)}\right] , \tag{50}$$

where $\phi$ denotes $\phi_{\text{st}}$. In the particular case when $R/P = 1$, we find that $(\Omega\phi) = B$; in that event, Eq. (50) reduces to

$$\Pi_{\text{st}}(x) \propto \exp\left[-\frac{\Omega x^2}{2B}\right] \ . \tag{51}$$

The exact probability distribution in this case is known to be the Poisson distribution,[7]

$$P_n = P_0 \frac{B^n}{n!} \tag{52}$$

which, for large $B$, does in fact reduce to the Gaussian distribution

$$P_n \propto \exp\left[-\frac{(n-B)^2}{2B}\right], \tag{53}$$

in agreement with (51).

### B. Case (b) $R/P=9$

This case is critical in that, with $B=\sqrt{27P}$, we obtain three identical roots: $(\Omega\phi_{1,2,3})=\sqrt{3P}$. This leads to $q=3$ and $p=0$, so that $\nu=\frac{3}{4}$. We note that, although $\nu=\frac{3}{4}$ here, the detailed situation of this case is very different from case II discussed in Sec. IV. The steady-state probability distribution is now given by

$$\Pi_{\rm st}(x)=\text{const}\exp\left[-\frac{\sqrt{3}\Omega^3x^4}{72P^{3/2}}\right], \tag{54}$$

with

$$\bar{x}=0,\quad [x^2]_{\rm av}=\left[\frac{72P^{3/2}}{\sqrt{3}\Omega^3}\right]^{1/2}\frac{\Gamma(\frac{3}{4})}{\Gamma(\frac{1}{4})}; \tag{55}$$

cf. Eqs. (42) and (43) of Sec. IV. A qualitatively similar situation will arise in the close neighborhood of the critical point, i.e., for $\Delta B=O(\Omega^{-1/4})$, except that $\bar{x}$ as well as $[x^2]_{\rm av}$ will be $O(1)$. Away from this neighborhood, the situation will be of the type discussed under case (a).

### C. Case (c) $R/P>9$

In this case we have three distinct real roots if $B_2<B<B_1$; here $B_1$ and $B_2$ are the turning points of the deterministic curve (48), shown as points $M$ and $N$ in Fig. 2. We find that

$$B_{1,2}^2=\frac{1}{8P}[(R^2+18RP-27P^2)\pm(R-P)^{1/2}(R-9P)^{3/2}]. \tag{56}$$

At points $L$ and $Q$ of the curve, $q=1$ and $p=0$, so that $\nu=\frac{1}{2}$ and the steady-state distribution is given by the Gaussian expression

$$\Pi_{\rm st}(x)\propto\exp\left[-\frac{9(B_i^2-3R)\Omega x^2}{8RB_i}\right]\quad(i=1,2). \tag{57}$$

At the turning points $M$ and $N$, $q=2$ and $p=0$, so that $\nu=\frac{2}{3}$ and the steady-state distribution turns out to be non-Gaussian:

$$\Pi_{\rm st}(x)\propto\exp\left[\frac{[(B_i^2-3R)]^{1/2}\Omega^2x^3}{2B_i(R-3P)}\right]\quad(i=1,2). \tag{58}$$

Of course, in these states the system is only marginally stable. In the region of three distinct roots, we have

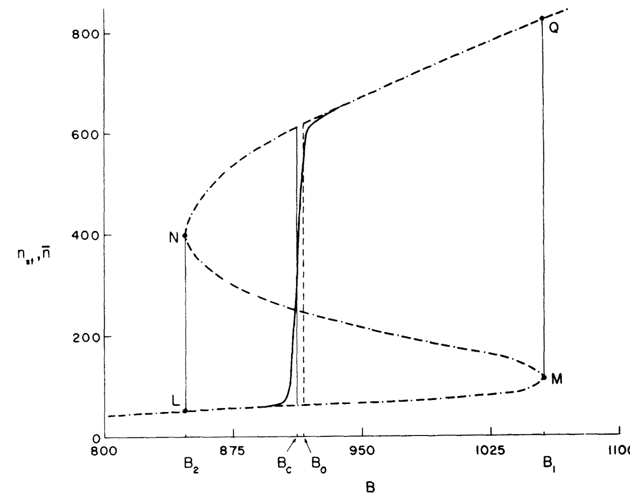


FIG. 2. Deterministic solution $n_{\rm st}$ as obtained from Eq. (48), —·—, and the stochastic mean $\bar{n}_{\rm st}$, as obtained from Eq. (63), ——, for $P=10^4$ and $R=2\times10^5$. Probabilistic construction yields $B_c\simeq912.3$ while the Maxwell-type construction yields $B_0\simeq916.1$

$$\Pi_{\rm st}(x)\propto\exp\left[-\frac{(\alpha_1-\alpha_2)(\alpha_1-\alpha_3)\Omega x^2}{2\alpha_1(\alpha_1+\alpha_2)(\alpha_1+\alpha_3)}\right] \tag{59}$$

on the lower branch, and

$$\Pi_{\rm st}(x)\propto\exp\left[-\frac{(\alpha_3-\alpha_1)(\alpha_3-\alpha_2)\Omega x^2}{2\alpha_3(\alpha_3+\alpha_1)(\alpha_3+\alpha_2)}\right] \tag{60}$$

on the upper branch; here, $\alpha_1<\alpha_2<\alpha_3$ are the roots of Eq. (48) arranged in the ascending order. It is obvious that the distributions (59) and (60) are local Gaussian distributions centered at $\alpha_1$ and $\alpha_3$, respectively; see Fig. 3. They may, in fact, be written as

$$\Pi_{\rm st}(n)\propto\exp\left[-\frac{(n-\alpha_1)^2}{2\sigma_1^2}\right] \tag{58$'$}$$

and

$$\Pi_{\rm st}(n)\propto\exp\left[-\frac{(n-\alpha_3)^2}{2\sigma_3^2}\right], \tag{59$'$}$$

where

$$\sigma_1^2=\frac{2\alpha_1(\alpha_1+\alpha_2)(\alpha_1+\alpha_3)}{(\alpha_1-\alpha_2)(\alpha_1-\alpha_3)}$$

and (61)

$$\sigma_3^2=\frac{2\alpha_3(\alpha_3+\alpha_1)(\alpha_3+\alpha_2)}{(\alpha_3-\alpha_1)(\alpha_3-\alpha_2)}.$$

It is well known that if there is only one stationary state accessible to the system then the probability distribution $\Pi_{\rm st}(n)$ possesses a sharp peak around $n=\Omega\phi_{\rm st}$ which, in the thermodynamic limit ($\Omega\to\infty$), tends to be a delta function at $n=\Omega\phi_{\rm st}$. In the present case $\Pi_{\rm st}(n)$ is *bimodal* over the entire interval $(B_2,B_1)$; see Fig. 3. As $B$ increases

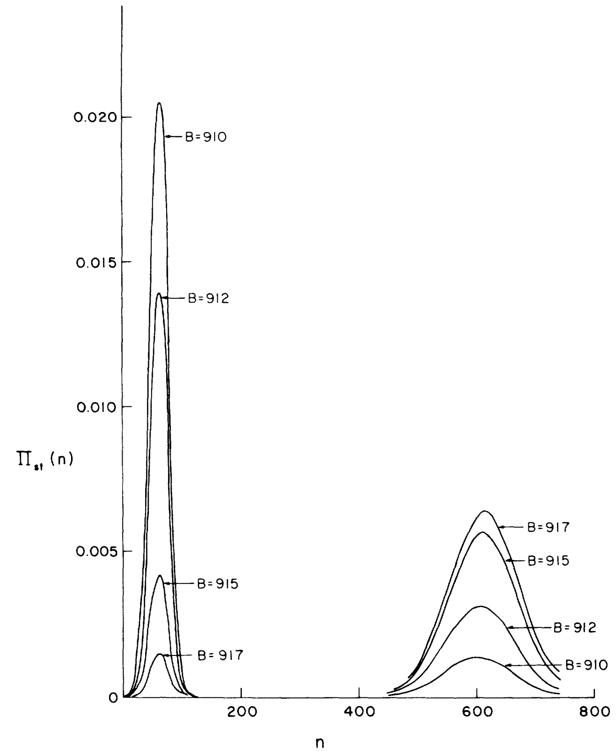


FIG. 3. Steady-state probability distribution $\Pi_{st}(n)$ for various values for the pump parameter $B$ in the vicinity of the critical value $B_c$.

from $B_2$ towards $B_1$, with fixed values of $R$ and $P$, the distribution $\Pi_{st}(n)$ continues to be dominant in the region around $n=\Omega\phi_1$ (i.e., $\alpha_1$) until $B$ enters the critical range $B \simeq B_c$ when the dominance shifts rapidly to the region around $n=\Omega\phi_3$ (i.e., $\alpha_3$), and the system jumps from the lower branch of Fig. 2 to the upper branch. With this in mind, $\Pi_{st}(n)$ may be written as

$$\Pi_{st}(n)=C_1\exp\left[-\frac{(n-\alpha_1)^2}{2\sigma_1^2}\right]+C_3\exp\left[-\frac{(n-\alpha_3)^2}{2\sigma_3^2}\right], \qquad (62)$$

where $C_1$ and $C_3$ are the "mixing coefficients" which vary critically with $B$. We thus obtain

$$\bar{n}=\pi_1\alpha_1+\pi_3\alpha_3 \qquad (63)$$

and

$$[n^2]_{av}=\pi_1(\alpha_1^2+\sigma_1^2)+\pi_3(\alpha_3^2+\sigma_3^2), \qquad (64)$$

where $\pi_1$ and $\pi_3$ are the probabilities associated with the regions around the macroscopic states $n=\alpha_1$ and $n=\alpha_3$, respectively:

$$\frac{\pi_1}{\pi_3}=\frac{C_1\sigma_1}{C_3\sigma_3}, \quad \pi_1+\pi_3=1 . \qquad (65)$$

We define $B_c$ as the value of $B$ for which

$$\pi_1=\pi_3=\tfrac{1}{2} \qquad (66)$$

so that

$$(\bar{n})_c=\tfrac{1}{2}(\alpha_1+\alpha_3) \qquad (67)$$

and

$$(\sigma_n^2)_c=\tfrac{1}{4}(\alpha_3-\alpha_1)^2+\tfrac{1}{2}(\sigma_1^2+\sigma_3^2) . \qquad (68)$$

For $B$ significantly less than $B_c$, $\pi_1 \simeq 1$ and $\pi_3 \simeq 0$, and for $B$ significantly greater than $B_c$, $\pi_1 \simeq 0$ and $\pi_3 \simeq 1$. Thus,

$$\bar{n} \simeq \begin{cases} \alpha_1(B) & \text{for } B_2<B<B_c \\ \alpha_3(B) & \text{for } B_c<B<B_1 \end{cases} \qquad (69)$$

and

$$[n^2]_{av} \simeq \begin{cases} \alpha_1^2(B)+\sigma_1^2(B) & \text{for } B_2<B<B_c \\ \alpha_3^2(B)+\sigma_3^2(B) & \text{for } B_c<B<B_1 . \end{cases} \qquad (70)$$

Combining Eqs. (63) and (64) we find that, in general,

$$\sigma_n^2=\pi_1\pi_3(\alpha_3-\alpha_1)^2+\pi_1\sigma_1^2+\pi_3\sigma_3^2 \qquad (71)$$

$$\simeq \begin{cases} \sigma_1^2=O(\Omega) & \text{for } B_2<B<B_c \\ \tfrac{1}{4}(\alpha_3-\alpha_1)^2+\tfrac{1}{2}(\sigma_1^2+\sigma_3^2)=O(\Omega^2) & \text{at } B=B_c \\ \sigma_3^2=O(\Omega) & \text{for } B_c<B<B_1 . \end{cases} \qquad (72)$$

Equation (72) shows quite clearly that in the vicinity of the critical point ($B \simeq B_c$) fluctuations become macroscopic—an essential ingredient of a phase transition. We also note the general relationship, which can be derived from the master equation itself, viz.,

$$B\frac{\partial \bar{n}}{\partial B}=\sigma_n^2 ; \qquad (73)$$

this shows how closely the rate of growth of the order parameter $\bar{n}$ with the pump parameter $B$ is related to the magnitude of the fluctuations in the system. It follows that in the vicinity of $B_c$, $\bar{n}$ rises steeply from a value close to $\alpha_1$ to a value close to $\alpha_3$, i.e., $\Delta\bar{n}=O(\Omega)$, over a range of $B$ which is only $O(1)$; see the solid curve in Fig. 2. We shall now carry out further analysis of the problem with the purpose of establishing a means of determining the precise value of $B_c$.

## VI. DETERMINATION OF $B_c$

Since we have defined $B_c$ in terms of the quantities $\pi_1$ and $\pi_3$, it is necessary to obtain explicit expressions for these quantities. In view of the fact that

$$\pi_1=\frac{C_1\sigma_1}{C_1\sigma_1+C_3\sigma_3} \quad \text{and} \quad \pi_3=\frac{C_3\sigma_3}{C_1\sigma_1+C_3\sigma_3}, \qquad (74)$$

and that explicit expressions for $\sigma_1$ and $\sigma_3$ are already known [see Eqs. (61)], we need only to know the ratio $C_1/C_3$.

Recalling that $n=0$ is a natural boundary of the process under study, the steady-state probability distribution $p_n$, as appearing in the master equation of the problem, and the corresponding potential function $\Phi_n$ [so that $p(n)=e^{-\Phi_n}$] are given by

$$p(n)=p_0\prod_{i=1}^{n}\left[\frac{\lambda_{i-1}}{\mu_i}\right] \tag{75}$$

and

$$\Phi_n=\text{const}+\sum_{i=1}^{n}\ln(\mu_i/\lambda_{i-1})\ . \tag{76}$$

Equation (75) is based on the fact that in its stationary state the system satisfies the principle of detailed balance, namely,

$$\mu_{n+1}p_{n+1}=\lambda_n p_n\ . \tag{77}$$

We note that at the turning points of the distribution $p_n=p_{n-1}$; these points are, therefore, determined by the condition $\lambda_{n-1}=\mu_n$, which leads to the "deterministic equation"

$$n^3-(B+3)n^2+(R+3B+2)n-(P+2)B=0\ ; \tag{78}$$

cf. Eq. (48). Now

$$\frac{C_1}{C_3}\equiv\frac{p(\alpha_1)}{p(\alpha_3)}=\exp[\Phi(\alpha_3)-\Phi(\alpha_1)]=\exp(E)\ , \tag{79}$$

for instance. We find that

$$\begin{aligned}E&=\sum_{i=\alpha_1}^{\alpha_3}\ln(\mu_i/\lambda_{i-1})\\&\simeq\int_{\alpha_1}^{\alpha_3}\ln\left[\frac{n[(n-1)(n-2)+R]}{B[(n-1)(n-2)+P]}\right]dn\\&=-(\alpha_3-\alpha_1)+\tfrac{3}{2}\ln\left[\frac{\alpha_3}{\alpha_1}\right]+2(R-\tfrac{1}{4})^{1/2}\left[\tan^{-1}\left[\frac{\alpha_3-\frac{3}{2}}{(R-\frac{1}{4})^{1/2}}\right]-\tan^{-1}\left[\frac{\alpha_1-\frac{3}{2}}{(R-\frac{1}{4})^{1/2}}\right]\right]\\&\quad-2(P-\tfrac{1}{4})^{1/2}\left[\tan^{-1}\left[\frac{\alpha_3-\frac{3}{2}}{(P-\frac{1}{4})^{1/2}}\right]-\tan^{-1}\left[\frac{\alpha_1-\frac{3}{2}}{(P-\frac{1}{4})^{1/2}}\right]\right]\ .\end{aligned} \tag{80}$$

Obviously, the definition of $B_c$ through Eq. (66) implies that the transition in question takes place when the area under the bimodal probability distribution curve divides itself equally between the regions around $n=\alpha_1$ and $n=\alpha_3$ (see Fig. 3). Denoting these areas by $\pi_1$ and $\pi_3$, respectively, we may write

$$\pi_1/\pi_3\equiv\exp(E')\ ,$$

so that

$$E'=\ln\left[\frac{C_1\sigma_1}{C_3\sigma_3}\right]=E+\tfrac{1}{2}\ln\left[\frac{\sigma_1^2}{\sigma_3^2}\right]\ . \tag{81}$$

Equations (61) and (80) completely determine $E'$ and hence the ratio $\pi_1/\pi_3$. We may now state that the transition from the lower to the upper branch of the curve in Fig. 2 takes place at that value of $B$ for which $E'=0$. This value of $B$ is indeed the one we have earlier called $B_c$. Taking $P=10^4$ and $R=2\times10^5$, we find that while $B_2=847.03$ and $B_1=1055.95$, $B_c$ turns out to be about 912.3.

## VII. THEOREM OF EQUAL AREAS

It is well known that the van der Waals equation of state is cubic in $v$ and, for $T<T_c$, its spinodal curve in the $p$-$v$ plane is an $S$-shaped curve, very much like the one we have in Fig. 2. There, the question as to which state on the lower branch of the curve would be in coexistence with the corresponding state on the upper branch of the curve is settled by the Maxwell's equal-area theorem.[31] The theorem states that a line parallel to the $v$ axis, which intercepts the $S$-shaped curve such that it encloses equal areas with the two segments of the curve, determines the states of coexistence. In the present problem, the turning points of the steady-state probability distribution satisfy the macroscopic equation

$$n^3-(B+3)n^2+(R+3B+2)n-(P+2)B=0\ , \tag{78}$$

which is also cubic in $n$. This equation, in fact, represents the hysteresis curve in the $(n-B)$ plane—a well-known characteristic of the first-order phase transitions (see Fig. 2). Impelled by this analogy, we thought it worthwhile to investigate the present problem as well along similar lines. The findings of this investigation turned out to be quite striking.

For a given value of $B$, for instance, $B'$ such that $B_2<B'<B_1$, the deterministic curve carves out two areas, which may be denoted by $A_1$ and $A_2$, respectively. Let $A_1$ be the area bounded by the line $B'$ and the deterministic curve between $B'$ and $B_1$ on the right, and $A_2$ the area bounded by the line $B'$ and the deterministic curve between $B'$ and $B_2$ on the left; then

$$A_1-A_2=\int_{\alpha_1'}^{\alpha_3'}[B(n)-B']dn\ , \tag{82}$$

where $\alpha_1'$ and $\alpha_3'$ are the smallest and the largest roots of Eq. (78) for $B=B'$ whereas $B(n)$ is the value of $B$ obtained from the equation of state (78) as a function of the variable $n$. Renaming the variables and using (78), we readily find that

$$\frac{A_1-A_2}{B}=\int_{\alpha_1}^{\alpha_3}\left[\frac{p(n-1)}{p(n)}-1\right]dn$$
$$=\int_{\alpha_1}^{\alpha_3}\left[\frac{n[(n-1)(n-2)+R]}{B[(n-1)(n-2)+P]}-1\right]dn$$
$$=-(\alpha_3-\alpha_1)+\frac{(\alpha_3^2-\alpha_1^2)}{2B}+\left[\frac{R-P}{2B}\right]\left\{\ln\left[\frac{(\alpha_3-1)(\alpha_3-2)+P}{(\alpha_1-1)(\alpha_1-2)+P}\right]\right.$$
$$\left.+\frac{3}{(P-\frac{1}{4})^{1/2}}\left[\tan^{-1}\left[\frac{\alpha_3-\frac{3}{2}}{(P-\frac{1}{4})^{1/2}}\right]-\tan^{-1}\left[\frac{\alpha_1-\frac{3}{2}}{(P-\frac{1}{4})^{1/2}}\right]\right]\right\}. \quad (83)$$

In the spirit of the theorem of equal areas, we define $B_0$ to be the value of $B$ for which $A_1=A_2$. We find that, for $P=10^4$ and $R=2\times10^5$, $B_0$ turns out to be 916.1, which is fairly close to the value of $B_c$ obtained in Sec. VI. In fact, using Newton's formula, we can write

$$B_c\simeq B_0-\frac{f(B_0)}{f'(B_0)},$$

where $f(B)$ and $f'(B)$ are implicit functions of $B$ as given by

$$f(B)\simeq-(\alpha_3-\alpha_1)-\tfrac{1}{2}\ln\left[\frac{\alpha_3(\alpha_3+\alpha_2)(\alpha_2-\alpha_1)}{\alpha_1(\alpha_1+\alpha_2)(\alpha_3-\alpha_2)}\right]$$
$$+2\sqrt{R}\left[\tan^{-1}\left[\frac{\alpha_3}{\sqrt{R}}\right]-\tan^{-1}\left[\frac{\alpha_1}{\sqrt{R}}\right]\right]-2\sqrt{P}\left[\tan^{-1}\left[\frac{\alpha_3}{\sqrt{P}}\right]-\tan^{-1}\left[\frac{\alpha_1}{\sqrt{P}}\right]\right]$$

and

$$f'(B)\simeq\frac{\alpha_1(\alpha_1+\alpha_2)(\alpha_1+\alpha_3)}{B(\alpha_1-\alpha_2)(\alpha_1-\alpha_3)}\left[1-\frac{2R}{R+\alpha_1^2}+\frac{2P}{P+\alpha_1^2}\right]-\frac{\alpha_3(\alpha_3+\alpha_1)(\alpha_3+\alpha_2)}{B(\alpha_3-\alpha_1)(\alpha_3-\alpha_2)}\left[1-\frac{2R}{R+\alpha_3^2}+\frac{2P}{P+\alpha_3^2}\right].$$

We observe that the function $f(B)$ changes rapidly, from positive values $O(\Omega)$ to negative values of the same order passing through the value zero as $B$ passes through $B_c$, whereas $f'(B)$ ocntinues to be of order unity. Accordingly, $B_0$ turns out to be very close to $B_c$. In fact, $B_0-B_c=O(1)$ and, in the limit $\Omega\to\infty$, $B_0/B_c\to1$. We thus find that the first-order phase transition of the type encountered here does indeed obey a theorem of equal areas which might hold for a much wider class of systems with cubic interactions. We cannot, however, accord this theorem a status comparable to the "Maxwell's theorem of equal areas" for physicochemical systems which rests on a much surer thermodynamic basis.

## VIII. CONCLUDING REMARKS

In line with our earlier work on nonlinear models with quadratic interactions which showed that, in spite of the fundamental differences in their structures, both open and closed systems are locally isomorphic in their critical regions, we have now analyzed a generalized nonlinear stochastic model with cubic interactions. A modified version of van Kampen's method of system-size expansion of the master equation has been employed to study the onset of a first-order phase transition in the system. While several features accompanying such a transition have been examined, a special effort has been made to answer the question as to when a general stochastic system with a bistable steady-state distribution will actually jump from one stable branch to another. While the true answer to this question lies in the probability distribution itself, a practical recipe in the form of a Maxwell-type theorem of equal areas is discovered. This theorem holds weakly for all finite systems with cubic interactions and attains full strength in the thermodynamic limit. We hope that the generalized model considered in this paper and the mathematical treatment developed here will provide a useful framework for similar studies relating to other scientific (and not-so-scientific) disciplines.

## ACKNOWLEDGMENT

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[1]P. Glansdorff and I. Prigogine, *Thermodynamic Theory of Structure, Stability and Fluctuations* (Wiley-Interscience, New York, 1971).

[2]I. Prigogine, in *Theoretical Physics and Biology,* edited by M. Marois (North-Holland, Amsterdam, 1969), pp. 162—185.

[3]R. Lefever and G. Nicolis, J. Theor. Biol. 30, 267 (1971).

[4]D. H. Sattinger, *Topics in Stability and Bifurcation Theory,* Vol. 309 of *Lecture Notes in Mathematics,* edited by A. Dold and B. Eckmann (Springer, Berlin, 1973).

[5]F. Schlögl, Z. Phys. 253, 147 (1972).

[6]A. Nitzan, P. Orteleva, J. Deutsch, and J. Ross, J. Chem. Phys. 61, 1056 (1974).

[7]J. Matheson, D. F. Walls, and C. W. Gardiner, J. Stat. Phys. 12, 21 (1976).

[8]I. Oppenheim, K. E. Shuler, and G. H. Weiss, Physica (Utrecht) 88A, 191 (1977).

[9]G. Nicolis and I. Prigogine, *Self-Organization in Nonequilibrium Systems* (Wiley-Interscience, New York, 1977).

[10]H. Haken, *Synergetics—An Introduction* (Springer, Berlin, 1978).

[11]I. Prigogine and R. Lefever, Adv. Chem. Phys. 29, 1 (1975).

[12]J. S. Turner, Adv. Chem. Phys. 29, 63 (1975).

[13]C. W. Gardiner, in *Stochastic Nonlinear Systems* (Springer, Berlin, 1981).

[14]L. Esaki, Science 183, 1149 (1974).

[15]A. van der Ziel, in *Solid State Physical Electronics,* 3rd ed. (Prentice-Hall, N.J., 1976).

[16]Y. Kobatake, Physica (Utrecht) 48, 301 (1970); Adv. Chem. Phys. 29, 319 (1975).

[17]R. Blumenthal, J. P. Changeux, and R. Lefever, J. Membr. Biol. 2, 351 (1970).

[18]R. A. Spangler and F. M. Snell, Nature 191, 457 (1961); J. Theor. Biol. 16, 381 (1967).

[19]B. B. Edelstein, J. Theor. Biol. 29, 57 (1970).

[20]J. Monod and F. Jacob, Cold Spring Harbor Symp. Quant. Biol. 26, 389 (1961).

[21]N. S. Goel, S. C. Maitra, and E. W. Montroll, Rev. Mod. Phys. 43, 231 (1971).

[22]R. M. May, *Model Ecosystems* (Princeton University, Princeton, N.J., 1973).

[23]D. F. Walls, Collect. Phenom. 2, 125 (1976).

[24]C. L. Sharma, R. K. Pathria, and Karmeshu, Phys. Rev. A 26, 3567 (1982).

[25]N. G. van Kampen, Can. J. Phys. 39, 551 (1961); Adv. Chem. Phys. 34, 245 (1976).

[26]N. G. van Kampen, *Stochastic Processes in Physics and Chemistry* (North-Holland, Amsterdam, 1981).

[27]R. F. Fox, J. Chem. Phys. 70, 4660 (1979).

[28]H. Dekker, J. Chem. Phys. 72, 189 (1980).

[29]R. Bellman, *Stability Theory of Differential Equations* (Dover, New York, 1969).

[30]I. S. Gradshteyn and I. M. Ryzhik, *Table of Integrals, Series and Products* (Academic, New York, 1980).

[31]R. K. Pathria, *Statistical Mechanics* (Pergamon, New York, 1972).