Fluctuations and transitions at chemical instabilities: The analogy to phase transitions*

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The properties of a reacting system near an instability are investigated and the analogy between transitions in unstable systems and equilibrium phase transitions is developed in detail. The set of macroscopic steady state rate equations plays the role of an equation of state. The bifurcation points of this set are analogous to transition and critical points of equilibrium phase transitions. Hard transitions of unstable systems correspond to first order and soft transitions to second and higher order phase transitions. Critical exponents are defined for those properties of the unstable systems which are singular at the transition points, and relations between these critical exponents are investigated. Critical fluctuations are studied with stochastic analogs of the macroscopic rate equations. Both master and Langevin equations are considered and lead to the following conclusions: When a transition or a critical point is approached (a) the amplitude of fluctuations grows; (b) the lifetime of these fluctuations becomes longer; and (c) the spatial correlation length increases. Our approximations are similar to those made in mean field theories of phase transitions and our results are thus "classical." However the critical exponents are not necessarily numerically identical to the Landau–Ginzburg exponents since they depend on the particular nonlinear system.

INTRODUCTION

The study of instabilities in chemical systems, like others such as in hydrodynamics, semiconductors, and electric circuits, is usually based on the phenomenological equations of motion commonly accepted for these systems. This reduces the problem to the stability of the solutions of nonlinear differential equations.[1] In addition, Glansdorff and Prigogine[2] have developed a thermodynamical approach in which the second variation of the local entropy plays the role of a Liapounoff function in studying the stability.

Recently some attention has been drawn to the close analogy between transitions in nonlinear systems which are studied as instabilities of the corresponding nonlinear differential equations, and phase transitions. In particular Graham and Haken,[3] and independently, DeGiorgio, Scully, Goldstein, and Lee,[4] have established the relationship between laser threshold and a critical point of a second order phase transition. On the other hand, the equations of motion of a single mode laser may be reduced to a set of coupled differential equations of the Van der Pol type.[5] These equations exhibit a transition from a steady state behavior to a limit cycle type oscillation at a given threshold value of a parameter which, in the laser case, corresponds to the pumping rate. Similarly, kinetic approaches to the Ising model also lead to nonlinear differential equations for the time evolution of the magnetization.[6] This equation possesses a bifurcation point where the steady state of zero magnetization becomes unstable and stable steady states of finite magnetization come into existence. These examples suggest a close analogy between transitions at bifurcation points of nonlinear equations of motion[7] and phase transitions.

The existence of this analogy has been suggested also in a few other works on instability phenomena. Zaitsev and Shliomis[8] and Boon[9] have considered this analogy for the onset of thermal convection in the Bénard problem. Pytte and Thomas[10] have studied it in their treatment of threshold phenomena in the Gunn effect in semiconductors. Similar considerations have been made by Landauer and Woo[11] for the case of tunnel diode circuits and for the problem of a parametrically excited subharmonic oscillator. Recently the analogy between transitions in nonlinear chemical rate models and phase transitions has been discussed by Schlogl[12a] and by Bienkowski and Skolnick.[12b] Some experimental work supports these theoretical studies. The increase in the amplitude of intensity fluctuations in lasers in the threshold region is well known.[13] Similar phenomena have been observed for noise in nonlinear electric circuits near the threshold of electrical oscillations.[14] In one case the existence of critical slowing down near such threshold has also been demonstrated.[15]

In this paper we present a detailed study of the analogy between phase transitions and instability phenomena. Though we use as example the theory of chemical instabilities, the treatment is general. It is applicable to any system whose macroscopic behavior is determined by nonlinear equations of motion and which undergoes a transition when one or more external parameters assume certain critical values. The properties of these systems near their marginal stability points (points for which linear stability analysis yields at least one root with a zero real part while the remaining roots have negative real parts) are studied by means of both the deterministic (averaged) macroscopic equations of motion and their stochastic analogs. The following points are discussed:

(a) The analogy between first and second order phase transitions and the corresponding hard and soft transitions between steady states of nonlinear differential equations is displayed in Sec. II.

(b) A treatment of the divergencies which occur when a system approaches a point of marginal stability and the "critical exponents" related to these divergencies is

presented in Sec. III.

(c) Stochastic analogs of the deterministic equations of motion are studied in Sec. IV. The concept of a steady state is reevaluated. In particular, the stochastic analog of a nonlinear differential equation which admits several stable steady states has only one (stable) steady state solution for the distribution function. Different macroscopic steady states are shown to correspond then to extremum points (maximum for stable and minimum for unstable steady states) of this distribution function. The properties of steady states and the meaning of transitions between them are discussed from this viewpoint. Also in Sec. IV we compare different approaches to the stochastic equations of motion. The results obtained from the phenomenological master equation are compared, for simple models, to those obtained by adding a stochastic source term to the macroscopic equation of motion (which yields a Langevin equation or an equivalent Fokker–Planck equation).

(d) The behavior of fluctations from the steady state when a system approaches marginal stability is discussed in Sec. V for a general system, using the linearized stochastic equations of motion. The phenomena of critical slowing down and the divergencies in the amplitude of fluctuations and in the spatial correlation length are studied. These divergencies are obviously a nonphysical outcome of a linear approximation, but they serve as indication of unusually large (though finite) fluctuations in the vicinity of bifurcation points.

II. TRANSITIONS AND CRITICAL POINTS

A first order phase transition is defined as a transition which involves a discontinuity in the state of the system and, as a result, in thermodynamic quantities like entropy, internal energy, and volume. In a second order phase transition the thermodynamic variables change continuously at the transition point while their derivatives, such as specific heat, are discontinuous. Usually also some symmetry property of the system is abruptly changed at a second order point.

Analogously, in the theory of instability in nonlinear differential equations one distinguishes between hard transitions and soft transitions which, as we shall see, are similar in nature to first and second order phase transitions. Adopting the language of chemical kinetics, the time evolution of a set of concentrations and other state variables ψ which determine the state of the system is given by

$$d\psi/dt = \mathbf{F}[\psi, \lambda] \ , \tag{II.1}$$

where λ is a set of external parameters or constraints like temperature or concentrations of particular chemical components, and where $\mathbf{F}$ is a nonlinear functional which contains the (assumed known) kinetics of the system under these prescribed constraints. The steady states of the system are the solution $\psi^0(\lambda)$ of

$$\mathbf{F}[\psi^0, \lambda] = 0 \ , \tag{II.2}$$

which constitutes the equation of state for the system under the constraints λ.

As $\mathbf{F}$ is nonlinear, more than one steady state solution $\psi^0(\lambda)$ is possible for Eq. (II.2). A given steady state may be stable or unstable according to whether a small arbitrary deviation from it decays to the original steady state or evolves away from it. When the parameters λ are changed continuously the system may reach a point λ^*, where the original steady state becomes unstable and a transition to a new branch of steady states occurs. Such a point is called a bifurcation or a transition point.

We define hard transitions between two steady state branches as transitions in which $\psi^0(\lambda)$ is discontinuous at $\lambda = \lambda^*$, that is the steady state concentrations are different in the two branches at the transition point. Soft transitions are transitions in which $\psi^0(\lambda)$ changes continuously but its derivative is discontinuous at the transition point.

A. Hard transitions

As a simple example consider the differential equation

$$dx/dt = F(x, \lambda) \tag{II.3}$$

with

$$F(x, \lambda) = -(x^3 - \mu x + \lambda) \ , \tag{II.4}$$

where μ is a positive constant and λ is an external parameter. The steady states of Eq. (II.3) are determined by the solution of the equation $F(x^0(\lambda), \lambda) = 0$; for the case Eq. (II.4) there will be one or three physical (i.e., real) roots depending on the value of λ. In Fig. 1 we plot the curve $y(x) = x^3 - \mu x$ and the horizontal line $y = -\lambda$. The steady states are given by the intersection points of these lines. For $|\lambda| > |\lambda^*| = (2/3)(\mu^3/3)^{1/2}$ there is only one steady state. For $|\lambda| < |\lambda^*|$ there are three steady states which lie on two stable branches and one unstable branch. The stability is determined as usual from linear analy-

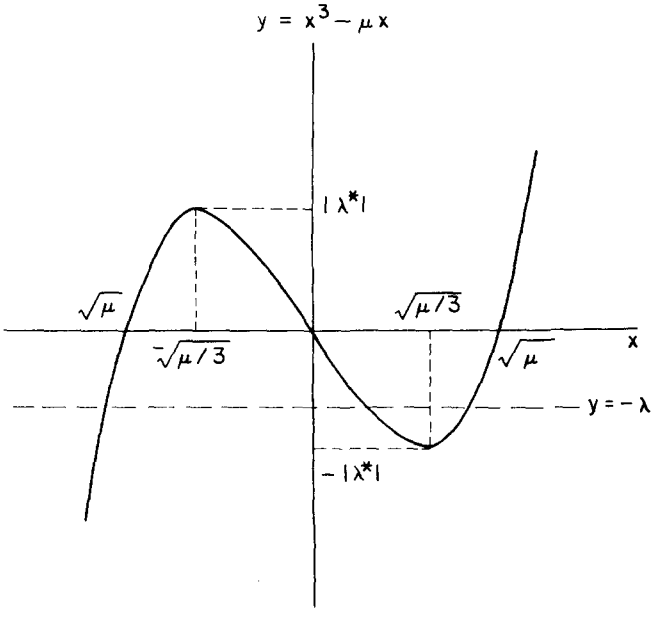


FIG. 1. The quantity $y = x^3 - \mu x$ displayed as a function of x. The crossing points with curves $y = -\lambda$ are the steady state of the system represented by the equation $x^3 - \mu x + \lambda = 0$. $\pm |\lambda^*|$ are the values of the parameter λ at the transition points.

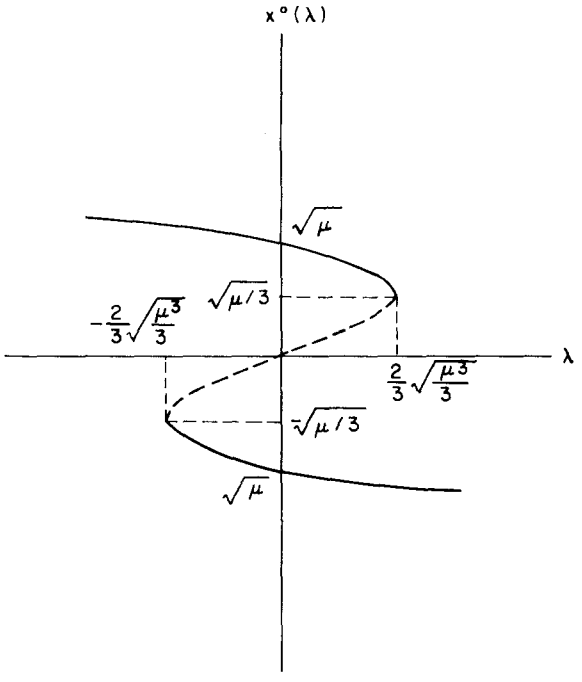


FIG. 2. The steady states $x^0(\lambda)$ of the system $x^3-\mu x+\lambda=0$ and their dependence on the parameter λ.

sis: Equation (II.3) linearized around a steady state gives

$$\frac{d\delta x}{dt}=-\left[\frac{d}{dx}(x^3-\mu x+\lambda)\right]_{x^0(\lambda)}\delta x \quad , \tag{II.5}$$

where $\delta x=x-x^0(\lambda)$. Thus

$$\left[\frac{d}{dx}(x^3-\mu x)\right]_{x^0(\lambda)}>0$$

corresponds to a stable steady state while the opposite inequality characterizes an unstable steady state.

A closer inspection of Fig. 1 reveals two important properties of the system described by Eq. (II.3): (a) $x^0(\lambda)$ is discontinuous at the transition points $\lambda^*=\pm(2/3)\times(\mu^3/3)^{1/2}$ and (b) hysteresis occurs when the direction of changing λ is reversed. These features are summarized in Fig. 2. Both features characterize also a first order phase transition. To have a better view of the analogy, Fig. 2 may be compared to Fig. 3 which describes the $P-V$ diagram (at constant T) of a liquid–gas phase transition.[16] Clearly the curve (a b c d e f) in Fig. 3 is analogous to the curve $x^0(\lambda)$ in Fig. 2; the stable branches (a b c) and (d e f) on which $(\partial P/\partial V)_T<0$ corresponds to the stable branches with $dx^0(\lambda)/d\lambda<0$, and the unstable branch with $(\partial P/\partial V)_T>0$ corresponds to the unstable branches with $dx^0(\lambda)/d\lambda>0$. In addition the hysteresis loop in Fig. 2 corresponds to the hysteresis loop in Fig. 3 which is known to exist in the liquid gas phase transition.

Despite this similarity between the two situations, an important difference should be made clear: in the liquid gas system the portions (b c) and (d e) of the $P-V$ curve correspond to thermodynamically metastable states, while the equilibrium transition occurs along the (b e) curve, constructed such that the chemical potential in the two phases is equal at equilibrium. No analogy to this construction exists in Fig. 2. However, the fact that the points c and d cannot be realized in practice also has its analogy in the case of Eq. (II.3): when noise and fluctuations (which always exist in physical systems) are included in Eq. (II.3), it will be shown (Sec. IV) that the transition points are not attainable and that transition will occur before they are reached. Moreover, as in the liquid–gas transition, the occurrence of hysteresis is an outcome of a relatively fast change of the parameter λ (which corresponds to P in Fig. 3) and if this change is made slow enough relative to the average lifetime of the metastable state no hysteresis loop should be observed. The problem remains whether in physical cases, where the macroscopic behavior is described by nonlinear equations of motion, and which exhibit transitions between different steady states and fluctuations around them, a construction analogous to the curve be in the PV diagram (Fig. 3) exists.

Continuing the discussion of the analogy, we note that as the points c and d in Fig. 3 correspond to a vanishing derivative of P with respect to V, $(\partial P/\partial V)_T=0$, similarly the marginal stability points correspond to

$$d\lambda/dx^0=0 \text{ (or } dx^0/d\lambda\to\infty) \quad . \tag{II.6}$$

In addition, the relation

$$\left(\frac{\partial F(x,\lambda)}{\partial x}\right)_{x_0(\lambda^*)}=0 \tag{II.7}$$

holds, where the derivatives are taken on the branch which becomes marginally stable.

In the case of liquid–gas phase transitions, on raising the temperature, a critical $P(V)$ curve is approached

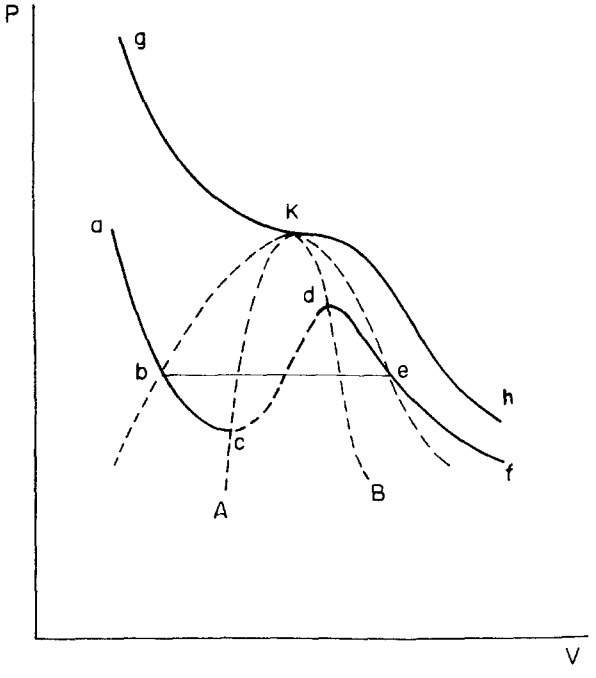


FIG. 3. A pressure (P), volume (V) diagram representing a liquid–gas phase transition.

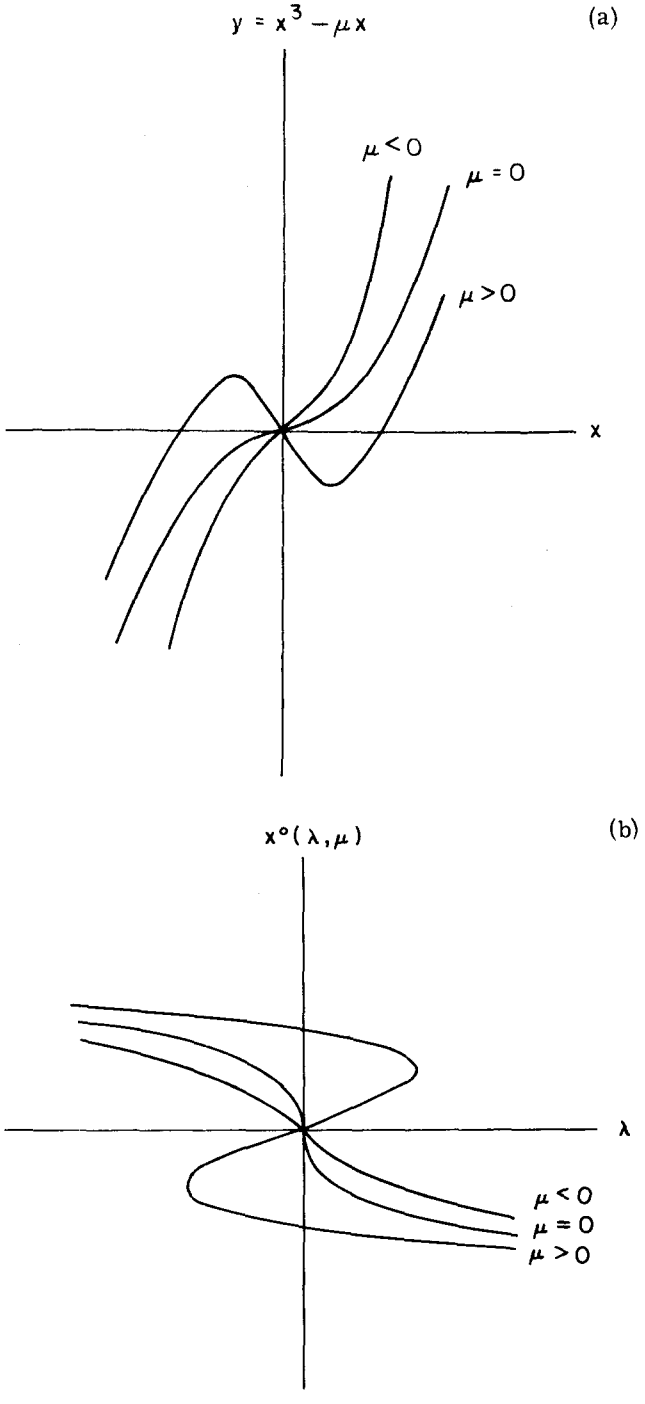


FIG. 4. The variation with μ of the equation of state represented in Figs. 1 and 2: (a) $y = x^3 - \mu x$ for different values of μ. (b) $x^0(\lambda, \mu)$ for different values of μ.

[curve (gkh) in Fig. 3] which passes through the critical point K; this point is characterized by the vanishing of both the first and the second derivatives of the pressure with respect to volume $(\partial P/\partial V)_{T_c} = (\partial^2 P/\partial V^2)_{T_c} = 0$. To explore this analogy for Eq. (II.3) we let μ also be a variable parameter and consider the equation of state $F(x, \lambda, \mu) = 0$ for different values μ (Fig. 4).

For $\mu > 0$ an unstable branch exists and two stable steady states might occur for the same "external conditions" μ and λ. For $\mu > 0$ only one (stable) steady state exists. The case $\mu = 0$ corresponds to the situation where the unstable branch has just disappeared. This is the only curve on which a point $(\lambda = 0, x^0 = 0)$ exists where $(\partial\lambda/\partial x^0)_\mu = [\partial^2\lambda/\partial(x^0)^2]_\mu = 0$. This point $\lambda_c = 0$, $\mu_c = 0$, $x_c = 0$ is the analog of a critical point in first order phase transition.

The similarity between the example given by Eq. (II.3) and first order phase transitions should not come as a surprise as our equation of state $x^3 - \mu x + \lambda = 0$ is identical to the classical equation of state of a liquid–gas system near the critical point [Ref. 16, Eq. (87.5)] or alternatively, to the van der Waals equation of state. However the analogy remains very much the same when more complicated systems with hard instability transitions are considered. A chemical example is provided by the Edelstein model[17]

$$\begin{aligned} &A + X \rightleftharpoons 2X \\ &X + E \rightleftharpoons C \\ &C \rightleftharpoons E + B \ , \end{aligned} \tag{II.8}$$

with A, B, E + C all constants. For this example the steady state equation is a cubic in the concentration X and the analysis is similar to the one presented above.

The examples given above together with many others may be summarized by the following general scheme: the system of equations of state obtained from Eq. (II.1)

$$F[\psi^0, \lambda, \mu] = 0 \tag{II.9}$$

may be used to eliminate all members of the vector ψ but one, which we shall denote x, and this leads to a reduced steady state equation

$$G[x^0, \lambda, \mu] = 0 \ , \tag{II.10}$$

where G is another nonlinear functional. A marginal stability point is given by[18]

$$\left(\frac{\partial\lambda}{\partial x^0}\right)_\mu = \left(\frac{\partial\mu}{\partial x^0}\right)_\lambda = 0 \ . \tag{II.11a}$$

The reciprocals of these derivatives are the analogs of thermodynamic susceptibilities. If

$$\left(\frac{\partial^2\lambda}{\partial(x^0)^2}\right)_\mu \ , \ \left(\frac{\partial^2\mu}{\partial(x^0)^2}\right)_\lambda \neq 0$$

we shall call this a transition point. This is the analog of points c and d in the phase diagram (Fig. 3). Note that Eq. (II.10) implies

$$\frac{dG}{dx^0} = \frac{\partial G}{\partial x^0} + \frac{\partial G}{\partial\lambda}\frac{\partial\lambda}{\partial x^0} + \frac{\partial G}{\partial\mu}\frac{\partial\mu}{\partial x^0} = 0$$

which together with Eq. (II.11a) leads to an equivalent condition for a marginal stability point

$$\left(\frac{\partial G}{\partial x^0}\right)_{\lambda,\mu} = 0 \ . \tag{II.11b}$$

A critical point is characterized by conditions (II.11) with the additional condition

$$\left(\frac{\partial^2\lambda}{\partial(x^0)^2}\right)_\mu = 0 \tag{II.12a}$$

or

$$\left(\frac{\partial^2 \mu}{\partial (x^0)^2}\right)_\lambda = 0 \qquad \text{(II.12b)}$$

provided third order derivatives are nonvanishing. The three conditions (II.10), (II.11), and (II.12a) or (II.12b) determine one or several points in the $x\lambda\mu$ space which are the critical points. These are the analogs of point K in Fig. 3. It should be mentioned that the two conditions (II.12a) and (II.12b) may be equivalent but unlike the conditions (II.11) this is not necessarily so. To see this we differentiate Eq. (II.10) twice with respect to x, at either constant λ or constant μ. Taking Eq. (II.11a) into account we get, for constant μ

$$\frac{\partial^2 G}{\partial (x^0)^2} + \frac{\partial G}{\partial \lambda}\frac{\partial^2 \lambda}{\partial (x^0)^2} = 0 \qquad \text{(II.13a)}$$

and for constant λ

$$\frac{\partial^2 G}{\partial (x^0)^2} + \frac{\partial G}{\partial \mu}\frac{\partial^2 \mu}{\partial (x^0)^2} = 0 \ . \qquad \text{(II.13b)}$$

From Eqs. (II.13a) and (II.13b) we obtain the interesting result that (provided $\partial G/\partial\mu$, $\partial G/\partial\lambda < \infty$ at the critical point)

$$\left(\frac{\partial^2 G}{\partial (x^0)^2}\right)_c = 0 \ . \qquad \text{(II.14)}$$

where the subscript c indicates the critical point. However, this does not imply that both $\partial^2\lambda/\partial(x^0)^2$ and $\partial^2\mu/\partial(x^0)^2$ are zero at this point, as $\partial G/\partial\lambda$ or $\partial G/\partial\mu$ (or both) may be zero there [in fact this was the case for the example given by Eqs. (II.3) and (II.4)].

In Appendix A we demonstrate the use of the general relations obtained here for a particular problem: instability in a chemically reactive illuminated system.

To end our discussion of hard transitions the following comments are in order:

(a) More than two external parameters are of course possible. Our discussion remains valid when variations in only two of these parameters are allowed. When this is not so and one considers spaces of higher dimensions the analogs of critical points of higher order are found. Without going into detail here, it is worthwhile to note that from

$$G(x^0, \lambda) = 0 \quad [\lambda = (\lambda_1, \lambda_2 \ldots)] \qquad \text{(II.15)}$$

we have

$$\left(\frac{\partial \lambda_i}{\partial \lambda_j}\right)_{x^0, \lambda_{k\neq i,j}} \left(\frac{\partial \lambda_j}{\partial x^0}\right)_{\lambda_{k\neq j}} = -\left(\frac{\partial \lambda_i}{\partial x^0}\right)_{\lambda_{k\neq i}} \qquad \text{(II.16)}$$

so that at a marginally stable point (and at a critical point of a first order transition) we have

$$\left(\frac{\partial \lambda_j}{\partial x^0}\right)_{\lambda_{k\neq j}} = 0 \qquad \text{(II.17)}$$

for every λ_j provided

$$\left(\frac{\partial \lambda_i}{\partial x_j}\right)_{x^0 \lambda_{k\neq ij}} \neq 0 \ , \qquad \text{(II.18)}$$

where λ_i is a parameter for which relation (II.17) is known a priori to hold. At marginal stability we have

$$\left(\frac{\partial G}{\partial x^0}\right)_\lambda = 0 \ ; \qquad \text{(II.19)}$$

moreover, at a critical point

$$\left(\frac{\partial^2 G}{\partial (x^0)^2}\right)_\lambda = 0 \ . \qquad \text{(II.20)}$$

It is worth noting that provided $(\partial G/\partial\lambda_j)_{x^0, \lambda_{i\neq j}} \neq 0$ for at least one i, then condition (II.19) is sufficient for a marginal stability point. This results from

$$\left(\frac{\partial G}{\partial x^0}\right)_\lambda + \left(\frac{\partial G}{\partial \lambda_j}\right)_{x^0, \lambda_{i\neq j}} \left(\frac{\partial \lambda_j}{\partial x^0}\right)_{\lambda_{i\neq j}} = 0$$

which is obtained from differentiating the equation of state with respect to x^0 keeping all $\lambda_i (i \neq j)$ constant. Similar reasoning shows that Eqs. (II.19) and (II.20) imply a critical point if $(\partial G/\partial\lambda_j)_{x^0, \lambda_{i\neq j}} \neq 0$ for that λ_j for which $\partial^2 x^0/\partial(\lambda_j)^2 = 0$ at the critical point, and provided that third order derivatives are nonzero.

(b) The conditions (II.10), (II.11), and (II.12) can be used to construct a form for the equation of state near the critical point if analytic behavior about this point is assumed. This equation is expected to be of the general form

$$G(\xi, l, m) = \xi^3 + f_1(l, m)\,\xi^2 + f_2(l, m)\,\xi + f_3(l, m) = 0 \ , \qquad \text{(II.21)}$$

where

$$\begin{aligned} \xi &= x - x_c \\ l &= \lambda - \lambda_c \\ m &= \mu - \mu_c \ . \end{aligned} \qquad \text{(II.22)}$$

From Eq. (II.10) we get $f_3(0,0) = 0$, Eq. (II.11b) gives $f_2(0,0) = 0$ and finally Eq. (II.14) implies that also $f_1(0,0) = 0$. Expanding the functions f_1, f_2, f_3 near the critical point then leads to

$$\xi^2 + (\alpha_1 l + \beta_1 m)\,\xi^2 + (\alpha_2 l + \beta_2 m)\,\xi + (\alpha_3 l + \beta_3 m) = 0 \ . \qquad \text{(II.23)}$$

If the critical point is such that $(\partial^2\mu/\partial x^2)_c \neq 0$ then in addition we have $(\partial G/\partial\mu)_c = 0$ or

$$\beta_3 = 0 \ . \qquad \text{(II.24)}$$

B. Soft transitions

As a simple example consider again Eq. (II.3) where now we take for $F(x, \lambda)$

$$F(x, \lambda) = -(x - \mu)^2 + \lambda(x - \mu) \qquad \text{(II.25)}$$

in which μ is a constant and λ is a variable parameter. There are two steady states

$$x^0 = \mu \ , \quad \mu + \lambda \ . \qquad \text{(II.26)}$$

These steady states and their stability (as obtained by linear stability analysis) are displayed in Fig. 5.

A different example which is closely related to the second order phase transition in a ferromagnet and to the laser threshold phenomenon is provided by

$$dx/dt = F(x, \lambda) = -[(x - \mu)^3 - \lambda(x - \mu)] \qquad \text{(II.27)}$$

which may have one or three real steady states according to whether λ is smaller or greater than zero. These

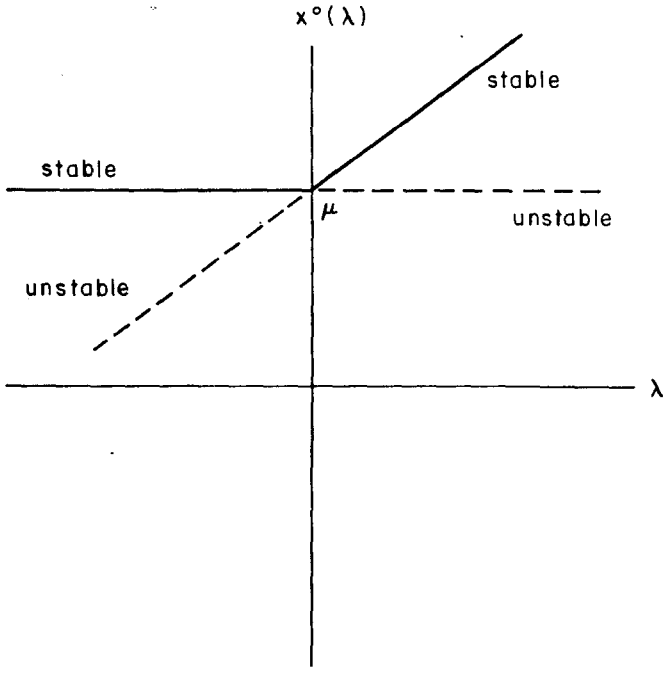


FIG. 5. Steady states of a system represented by Eq. (II.25).

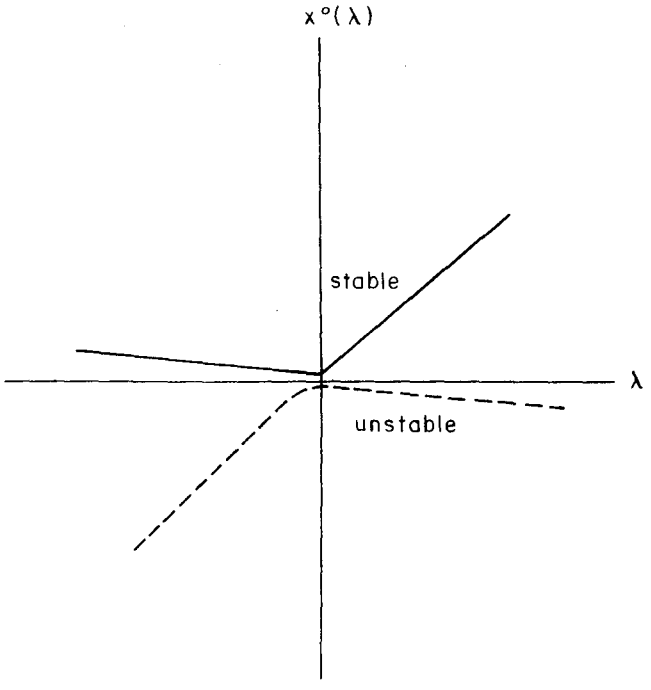


FIG. 7. Steady states of the system (II.28) with the reverse of the second equation included.

states with their stability are shown in Fig. 6.

A "chemical" example is provided by the following sequence of reactions

$$\begin{aligned} &A + C + X \rightleftharpoons A + 2X \\ &X \rightarrow Y + B \end{aligned} \qquad \text{(II.28)}$$

where the second reverse reaction is neglected. The rate equation is

$$dX/dt = -AX^2 + (AC - 1)X \qquad \text{(II.29)}$$

or, putting $\gamma = tA$ and $\lambda = (AC - 1)/C$,

$$dX/d\gamma = -X^2 + \lambda X \qquad \text{(II.30)}$$

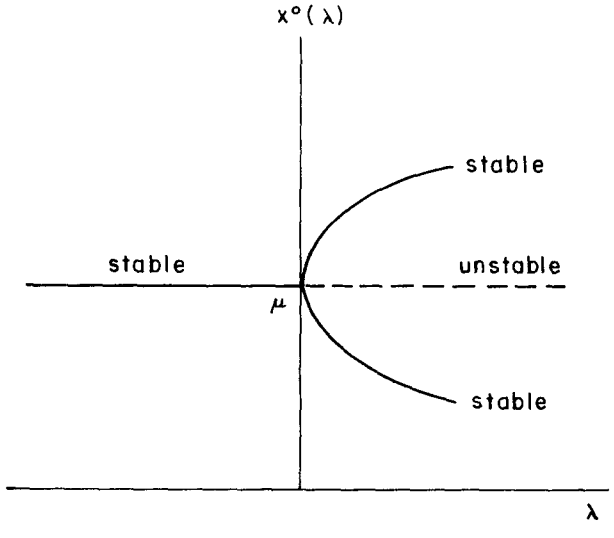


FIG. 6. Steady states of a system represented by Eq. (II.27).

which is identical with the situation represented by Fig. 5. It is however important to note that when slow reverse reactions are included in Eq. (II.28) the corrected steady states curve do not cross and the new situation is as given by Fig. 7.[19]

The examples presented here reflect the analogy between soft transitions in instability theory and second order phase transitions. Two important features are evident in all these cases: (a) $x^0(\lambda)$ is continuous at the transition point $\lambda = \lambda^* = 0$, but its derivative is not; (b) no ambiguity about the actual transition point exists and no hysteresis appears. Hence we cannot distinguish here between a transition point and a critical point as in the case of hard transitions and, more important, a soft transition point is expected to be experimentally achievable.

Hopf[20] has analyzed the case in which a steady state becomes unstable at λ^*, with the real part of a complex conjugate pair of eigenvalues vanishing linearly in $(\lambda - \lambda^*)$ (critical exponent one) near λ^*. Under this circumstance, for a broad class of nonlinearities which balance off the "linearized" growth, a family of limit cycles bifurcates beyond $\lambda > \lambda^*$ with amplitude varying as $(\lambda - \lambda^*)^{1/2}$ (with critical exponent 1/2). Many of the general theorems studied above can be extended to this and other cases of bifurcating cycles.

III. CRITICAL EXPONENTS

The analogy between transitions in nonequilibrium systems and phase transitions suggests that one may investigate divergencies and critical exponents in much the same way as in thermodynamic critical points. We also show the relationship between the steady state divergencies and the conditions for marginal stability ob-

tained from a linear analysis. The analysis given here is based on the assumption that the kinetic equations hold up to the transition point itself. Experimental measurement of critical exponents is necessary for verifying this assumption.

A. First order (hard) transitions

The equations of motion are again represented by Eq. (II.1) and the steady state equation is

$$F[\psi^0(\lambda), \lambda] = 0 \quad . \tag{III.1}$$

The system is assumed to have transition points and critical points. As was noted in the previous section only the latter are expected to be experimentally achievable The discussion in this section applies equally to both types and arbitrarily we shall use the term critical points.

Let λ_1 be one of the external parameters. A first order transition point is characterized by the divergency of the derivative of the vector $\psi^0(\lambda)$ with respect to λ_1. Let λ_a denote the direction of approach to the critical point [that is λ_a approaches its critical value while all $\lambda_j (j \neq a)$ are maintained at their critical values]. Then we can write

$$\left(\frac{\partial \psi^0(\lambda)}{\partial \lambda_1}\right)_a = \frac{A_1^{(a)}(\lambda_a)}{\lambda_a^{\alpha_a}} \quad ; \quad \alpha_a > 0 \tag{III.2}$$

where, for brevity, we take the values of all (λ_i) to be zero at the critical point considered, and where $(\partial/\partial\lambda_j)_a$ denotes a derivative evaluated at $\lambda_i = 0$ for every $i \neq a$ and $\lambda_a \neq 0$. $A_1^{(a)}(\lambda_a)$ is a vector which may depend on λ_a but remains finite when $\lambda_a \to 0$.

Equation (II.16), in which x may be replaced by any of the components of ψ^0 implies that for every λ_j for which at the critical point

$$\left(\frac{\partial \lambda_1}{\partial \lambda_j}\right)_{\lambda_{i\neq 1,j}} = \frac{(\partial G/\partial \lambda_j)_{\lambda_{i\neq j}}}{(\partial G/\partial \lambda_1)_{\lambda_{i\neq j}}} \neq 0 \tag{III.3}$$

we have

$$\left(\frac{\partial \psi^0(\lambda)}{\partial \lambda_j}\right)_a = \frac{A_j^{(a)}(\lambda_a)}{\lambda_a^{\alpha_a}} \tag{III.4}$$

with the same α_a as in Eq. (III.2) and with

$$\left(\frac{\partial \lambda_1}{\partial \lambda_j}\right)_a A_j^{(a)}(\lambda_a) = A_1^{(a)}(\lambda_a) \quad . \tag{III.5a}$$

In particular, at the critical point itself Eq. (III.5a) may be recast in the form

$$\left(\frac{\partial \lambda_1}{\partial \lambda_j}\right)_c A_j^{(a)}(0) = A_1^{(a)}(0) \quad . \tag{III.5b}$$

After estabishing these points it will be sufficient to define a critical exponent in terms of only two parameters: λ_1 with respect to which derivatives are taken and λ_a which determine the direction of approach. Of course $\lambda_1 = \lambda_a$ is a possible case.

Besides the divergency represented in Eq. (III.2), the system has another singularity at the critical point which manifests itself by the vanishing[21a] of at least one eigenvalue of the matrix $\Omega(\lambda)$ defined by

$$\Omega(\lambda) = \left(\frac{\partial \mathbf{F}(\psi, \lambda)}{\partial \psi}\right)_{\lambda, \psi^0(\lambda)} \quad . \tag{III.6}$$

It is interesting to study the relation between this singularity and the divergency of $\partial\psi^0(\lambda)/\partial\lambda_1$ and between the critical exponents involved. To this end we start from Eq. (III.1) in the form

$$F[\psi^0(\lambda_1, \lambda_a), \lambda_1, \lambda_a] = 0 \quad , \tag{III.7}$$

where $\lambda_i = 0$ (for $i \neq 1, a$) and are no longer considered explicitly. From now on we shall also omit the subscript a which specifies the direction of approach to the critical point, while keeping in mind that such specification is implied. Taking the derivative of Eq. (III.7) with respect to λ_1 at the point $\lambda_1 = 0$, $\lambda_a = \lambda \neq 0$[21b] we get

$$\Omega(\lambda)\left(\frac{\partial \psi^0}{\partial \lambda_1}\right)_{\lambda_1=0} + \left(\frac{\partial \mathbf{F}}{\partial \lambda_1}\right)_{\lambda_1=0} = 0 \tag{III.8}$$

or, using Eq. (III.2)

$$\Omega(\lambda)\mathbf{A}_1(\lambda) = -\lambda^{\alpha}\mathbf{B}_1(\lambda) \quad , \tag{III.9}$$

where the vector

$$\mathbf{B}_1(\lambda) = \left(\frac{\partial \mathbf{F}}{\partial \lambda_1}\right)_{\lambda_1=0} \tag{III.10}$$

is expected to remain nonzero and finite at the critical point $(\lambda = 0)$. Now expand the vectors $\mathbf{A}(\lambda)$ and $\mathbf{B}(\lambda)$ in the set of right eigenvectors $\phi_n(\lambda)$ of the matrix $\Omega(\lambda)$

$$\Omega(\lambda)\phi_n(\lambda) = z_n(\lambda)\phi_n(\lambda) \quad , \tag{III.11a}$$

$$\mathbf{A}_1(\lambda) = \sum_n a_n(\lambda)\phi_n(\lambda) \quad , \tag{III.11b}$$

$$\mathbf{B}_1(\lambda) = \sum_n b_n(\lambda)\phi_n(\lambda) \quad . \tag{III.11c}$$

Inserting Eqs. (III.11) into Eq. (III.9) and taking the scalar product with the nth left eigenvector $\Omega(\lambda)$, we obtain

$$z_n(\lambda)a_n(\lambda) = -\lambda^{\alpha} b_n(\lambda) \quad . \tag{III.12}$$

Assuming that none of the quantities $z_n(\lambda)$, $a_n(\lambda)$, and $b_n(\lambda)$ diverge when $\lambda \to 0$, we can write quite generally

$$b_n(\lambda) = \xi_{1n}\lambda^{\beta_n} \tag{III.13a}$$

$$a_n(\lambda) = \xi_{2n}\lambda^{\gamma_n} \tag{III.13b}$$

$$z_n(\lambda) = \xi_{3n}\lambda^{\delta_n} \quad , \tag{III.13c}$$

where $\beta_n, \gamma_n, \delta_n \geq 0$ and where $\xi_{3n} < 0$. $\xi_{in} (i = 1, 2, 3)$ remain finite when $\lambda \to 0$. We thus obtain

$$\delta_n + \gamma_n = \alpha + \beta_n \quad . \tag{III.14}$$

Usually $\delta_n = 0$ for most of the roots but we know that there is at least one root which becomes zero at the critical point. Such "unstable roots" are denoted by the index u so that

$$\delta_u > 0$$

$$\delta_n = 0 \text{ for } n \neq u \quad . \tag{III.15}$$

Hence, for $n \neq u$ we have

$$\gamma_n = \alpha + \beta_n > 0 \tag{III.16}$$

which [from (III.11b) and (III.13b)] means that eigenvec-

tors which belong to stable roots do not contribute to the vector $\mathbf{A}(0)$. This vector is thus an eigenvector of $\mathbf{\Omega}(0)$ with the eigenvalue zero. [This is of course also clear from Eq. (III.9).] For unstable roots we have

$$\gamma_u = \alpha + \beta_u - \delta_u \quad . \tag{III.17}$$

We know that there is at least one γ_u which is zero [as $\mathbf{A}(\lambda)$ must remain nonzero when $\lambda \to 0$]. In the usual case when there is only one unstable root, the corresponding γ_u must be zero. In this case

$$\delta_u = \alpha + \beta_u \geq \alpha \quad . \tag{III.18}$$

This is an inequality among the critical exponents which states that the rate at which the unstable root vanishes is at least as fast as the rate at which $(\partial\psi/\partial\lambda)$ diverges when $\lambda \to 0$. Often β_u will vanish in which case $\delta_u = \alpha$. We stress again that all these critical exponents are evaluated for a particular direction of approach to the critical point and may depend on this direction.

Finally it is important to note that like in other theories of this kind (e.g., Landau theory of second order phase transitions) which neglect the effect of fluctuations on the critical exponents, our theory will usually predict "classical" exponents. For example, the relation between λ and X^0 near a transition point,

$$\lambda = \lambda^* + \frac{1}{2}\frac{\partial^2\lambda}{\partial(x^0)^2}(x^0 - x^{0*})^2 + \ldots \quad , \tag{III.19}$$

which describes the extremal behavior (e.g., Fig. 2) at the transition point, leads to

$$\partial x^0/\partial\lambda \sim (\lambda - \lambda^*)^{-1/2} \tag{III.20}$$

about this point. At the critical point $\partial^2\lambda/\partial(X^0)^2$ may be zero and critical exponent 1/3 is then obtained.

B. Second order (soft) transitions

Here $\psi^0(\lambda)$ is continuous at the transition point but $\partial\psi^0/\partial\lambda$ is not. We consider two cases: (a) $\partial\psi^0/\partial\lambda$ is finite at the transition point but undergoes a finite jump; (b) $\partial\psi^0/\partial\lambda$ is infinite for one of the branches at transition (transition to a soft limit cycle is included in this class). We show that both cases imply a marginal stability root at the transition point. For simplicity we consider one external parameter λ.

Case (a). Taking the derivative of Eq. (III.1) with respect to λ we obtain

$$\mathbf{\Omega}^i(\lambda)\left(\frac{\partial\psi^i}{\partial\lambda}\right) + \frac{\partial\mathbf{F}[\psi^i, \lambda]}{\partial\lambda} = 0 \quad , \tag{III.21}$$

for each of the two branches $i = 1, 2$ which exchange stability at the critical point. At this point both $\mathbf{\Omega}^i(\lambda^*)$ and the second term on the lhs of Eq. (III.21) are the same for the two branches since $\psi^1(\lambda^*) = \psi^2(\lambda^*)$. Thus taking

$$\mathbf{\Delta}(\lambda) = \frac{\partial}{\partial\lambda}(\psi^1(\lambda) - \psi^2(\lambda)) \quad , \tag{III.22}$$

Eq. (III.21) leads to

$$\mathbf{\Omega}(\lambda^*)\,\mathbf{\Delta}(\lambda^*) = 0 \quad . \tag{III.23}$$

Hence, the stability matrix $\mathbf{\Omega}$ has at least one zero eigenvalue at $\lambda = \lambda^*$ and a corresponding eigenvector parallel to the discontinuity vector $\Delta(\lambda^*)$. Taking the two sets of eigenvectors $(\phi_n^i(\lambda))$ of $\mathbf{\Omega}^i(\lambda)$ $(i = 1, 2)$

$$\mathbf{\Omega}^i(\lambda)\,\phi_n^i(\lambda) = z_n^i(\lambda)\,\phi_n^i(\lambda) \tag{III.24}$$

we may expand in terms of these eigenvectors to obtain

$$z_n^i(\lambda)\,e_n^i(\lambda) = -\,b_n^i(\lambda) \quad , \tag{III.25}$$

where

$$\frac{\partial\psi^i}{\partial\lambda} = \sum_n e_n^i(\lambda)\,\phi_n^i(\lambda) \tag{III.26}$$

$$\frac{\partial\mathbf{F}[\psi^i, \lambda]}{\partial\lambda} = \sum_n b_n^i(\lambda)\,\phi_n^i(\lambda) \quad . \tag{III.27}$$

With $\lambda^* = 0$ we can write in the vicinity of the critical point

$$\begin{aligned} z_n^i(\lambda) &\sim \lambda^{\delta_n^i} \\ e_n^i(\lambda) &\sim \lambda^{\epsilon_n^i} \\ b_n^i(\lambda) &\sim \lambda^{\beta_n^i} \end{aligned} \tag{III.28}$$

so that

$$\delta_n^i + \epsilon_n^i = \beta_n^i \quad . \tag{III.29a}$$

For the unstable root $n = u$ we expect that ϵ_u^i will be zero at least for one of the branches. In this case we have

$$\delta_u^i = \beta_u^i \quad . \tag{III.29b}$$

Case (b). If $\partial\psi^i/\partial\lambda$ is infinite for the branch i at the transition point, Eq. (III.21) implies that there must be at least one associated zero eigenvalue of $\mathbf{\Omega}(\lambda^*)$ (assuming $\partial F/\partial\lambda$ is finite at $\lambda = \lambda^*$). The analysis of critical indices is similar to that for hard transitions.

Consider now a transition from a steady state to a soft cycle. Let us briefly consider the relationship between the amplitude of the bifurcating cycle and the stability properties of the system. Taking the derivative of the kinetic equation (II.1) with respect to λ we obtain

$$\frac{\partial}{\partial t}\left(\frac{\partial\psi}{\partial\lambda}\right) = \mathbf{\Omega}\,\frac{\partial\psi}{\partial\lambda} + \frac{\partial\mathbf{F}}{\partial\lambda} \quad , \tag{III.30}$$

where $\mathbf{\Omega} = (\partial F/\partial\psi)$ is to be evaluated at the limit cycle and is thus time dependent. If the amplitude of the cycle increases from zero at λ^* with infinite slope (typically as $(\lambda - \lambda^*)^{1/2}$)[7,20] then, assuming $(\partial F/\partial\lambda)$ to be finite and noting that at λ^* the matrix $\mathbf{\Omega}$ becomes simply the matrix determining the stability of the steady state, we see that the stability analysis for the steady state yields a pair of conjugate pure imaginary roots at λ^*. [This is seen by comparing the coefficients of the divergent left and first right hand terms in (III.30) at λ^*.]

C. Divergence of penetration length

The mathematical feature common to all types of transitions from a steady state to another steady state or to a limit cycle is the vanishing of the real part of a root of the matrix $\mathbf{\Omega}(\lambda)$ defined in Eq. (III.6) as $\lambda \to 0$. In this section we have established the relation between this phenomenon and the singularity in (III.2) for the case where the vanishing root is real. In the following sections we shall study the relation between this approach

to zero and fluctuation phenomena. For completeness we mention here the penetration of boundary perturbations[22] into a system in which diffusion and nonlinear chemical processes occur simultaneously. The kinetic equations take the form,

$$\frac{\partial \psi}{\partial t} = \mathbf{D}\nabla^2 \psi + \mathbf{F}[\psi, \lambda] \quad , \tag{III.31}$$

where $\mathbf{D}$ is a matrix of diffusion coefficients. The penetration vectors $\mathbf{k}$ are obtained as solutions to the equation

$$\det\{k^2 \mathbf{D} - [\Omega(\lambda) - i\omega \mathbf{1}]\} = 0 \quad , \tag{III.32}$$

where ω is the frequency of the applied perturbation which penetrates like $\exp(i\mathbf{k}\cdot\mathbf{r})$. For the simplest case of equal and diagonal diffusion coefficients $D_{ij} = D\delta_{ij}$, the penetration length for the mode m is obtained in the form

$$\Delta_m = \frac{1}{\mathrm{Im}(k_m)} = \left(\frac{D}{-\mathrm{Re}z_m(\lambda)}\right)^{1/2} \quad , \tag{III.33}$$

where $z_m(\lambda)$ is the mth eigenvalue of the matrix $\Omega(\lambda)$. For the unstable roots u, Δ_u diverges like $[\mathrm{Re}z_u(\lambda)]^{-1/2}$. Equations (III.18) and (III.20) imply that the associated critical exponent is $\delta_u \geq 1/4$ where the last inequality is introduced for typical case ($a = 1/2$) as discussed below Eq. (III.19).

D. Long time tails

At the transition point the dynamics of even small perturbations is determined by the nonlinearities since at this point the linear analysis yields at least one stability eigenvalue having zero real part. The evolution of small perturbations at the transition point is thus not simply exponential but may involve long-time contributions decaying with some inverse power of the time.

To illustrate this phenomenon consider the model system (II.23) at $\mu = 0$;

$$dx/dt = \lambda x - x^2 \quad . \tag{III.34}$$

This system has soft transition at $\lambda = 0$ from the $x^0 = 0$ branch to the $x^0 = \lambda$ branch. For arbitrary initial condition $x(t=0) \equiv x(0)$ this system may be solved exactly as follows:

$$x(t, \lambda) = \frac{x(0)\, e^{\lambda t}}{1 + x(0)\,[(e^{\lambda t} - 1)/\lambda]} \quad . \tag{III.35}$$

We see that small amplitude perturbations from the null state $x(0) \ll 1$, evolve according to $x(0)e^{\lambda t}$ for $\lambda < 0$ as expected from a linear analysis. However, at the transition point $\lambda \to 0$ we obtain

$$x(t, \lambda = 0) = x(0)\,[1 + x(0)t]^{-1} \quad . \tag{III.36}$$

For $\lambda = 0$ we see a slow decay proportional to t^{-1} which is shown below to be typical of the effect of a second order nonlinearity at the transition point.

If $x(0) < 0$ we see that $x(t)$ diverges as t goes to $-[x(0)]^{-1}$. This corresponds to the instability of the system to negative perturbation in x. For $\lambda < 0$, x also grows if $x(0) < \lambda < 0$.

Consider a system evolving according to (II.1). We take the system to have a single (stability) eigenvalue which vanishes at the transition. Let us introduce the deviation $\chi'(t, \lambda)$ from the steady state,

$$\chi'(t, \lambda) = \psi(t, \lambda) - \psi^0(\lambda) \tag{III.37}$$

in terms of which the rate equation (II.1) becomes

$$d\chi'/dt = \Omega(\lambda)\chi' + \mathbf{N}'[\chi', \lambda] \quad , \tag{III.38}$$

where Ω is the stability matrix [see (III.7)] and $\mathbf{N}'$ is the nonlinear contribution (in χ') to $\mathbf{F}$. It is convenient to transform variables to a new set χ, constructed from (λ dependent) linear combinations of the χ', which leave $\Omega(\lambda)$ diagonal. Thus for component n of χ we have

$$d\chi_n/dt = z_n(\lambda)\,\chi_n + N_n[\chi, \lambda] \quad , \tag{III.39}$$

where N_n is the nth component of the nonlinearity, transformed according to the similarity transformation which diagonalizes Ω and alters χ' into χ. If at the transition point λ^* the particular root $n = u$ vanishes then we have

$$d\chi_u/dt = N_u \chi[\chi, \lambda^*] \quad . \tag{III.40}$$

Now if we assume that N_u is second order in χ_u and second or higher order in the other components of χ then we show that the long time behavior of χ_u must be t^{-1}, assuming that $\mathrm{Re}z_n < 0$ for $n \neq u$, and that χ may be expanded in inverse powers of t.

We take

$$N_u[\chi, \lambda^*] = B_u(\lambda^*)\,\chi_u^2 + \Delta N_u[\chi, \lambda^*] \quad , \tag{III.41}$$

where ΔN_u contains only second order terms in $\chi_{n\neq u}$ (or their products with χ_u) and third or higher order terms in χ_u. As $t \to \infty$, decaying perturbations in χ_u must obey

$$\chi_u(t, \lambda^*) \sim \chi_u(0, \lambda^*)\,[1 - B_u \chi(0, \lambda^*)t]^{-1} \quad . \tag{III.42}$$

Since $z_{n\neq u}$ does not vanish, the dominant contribution to $\chi_{n\neq u}$, as obtained from the solution of

$$d\chi_n/dt = z_n(\lambda)\,\chi_n + B_n\,\chi_u^2 + \Delta N_n[\chi, \lambda] \tag{III.43}$$

is of order t^{-2} as $t \to \infty$. Taking an asymptotic expansion in the form of inverse powers of t as $t \to \infty$ and using (III.42) we find from (III.43) that χ_n has the limiting behavior

$$\chi_{n\neq u} \underset{t\to\infty}{\sim} -(B_n/z_n B_u^2)\, t^{-2} \quad . \tag{III.44}$$

As in the simple example (III.34) these results on the regression of fluctuations hold only in one polarity of the perturbation [$B_u \chi_u(0)^* < 0$]. In the opposite case χ_u grows and couples strongly to the other variables $\chi_{n\neq u}$.

To end this section we note that many of the results presented here can be extended to transitions between states of inhomogeneous systems.

IV. FLUCTUATIONS

In this and the next section we consider stochastic analogs of the macroscopic equations of motion in order to study fluctuations from steady states,[23] in particular when the system approaches a critical point. (Again, if not explicitly said otherwise, statements about critical points apply also to transition points.) We limit ourselves to fluctuations in those macroscopic quantities

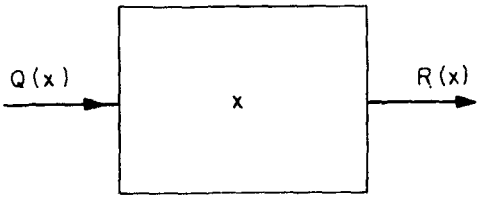


FIG. 8. Model for nonlinear kinetic systems with one variable.

which are influenced by the approach to instability and to time scales which are inherent in the macroscopic equations of motion for these quantities. We neglect fluctuations from local equilibrium (which, as usual, is assumed to exist) which occur on a much shorter time scale. In the chemical case we shall thus limit ourselves to fluctuations which occur on the chemical and hydrodynamic time scales, taking the corresponding transport coefficients (like chemical rate and diffusion coefficients) as constants. We shall be concerned with the effects of approaching a critical point on (a) the amplitude of these fluctuations, (b) the rate of regression of these fluctuations, and finally (c) the spatial correlation length. In analogy to phase transitions we expect an increase in all these quantities in the vicinity of a critical point. As in thermodynamical critical points we shall find that these quantities diverge in a linear approximation, but remain finite (and large) when nonlinear corrections are included.

No first principle microscopic theory exists for fluctuations in reacting chemical systems. We shall utilize the conventional approach of writing a phenomenological master equation based on the macroscopic rate equations. Alternatively one can consider a Langevin equation obtained by adding stochastic source terms to the macroscopic rate equations. If these terms are taken as Gaussian stochastic variables one can then consider the equivalent Fokker–Planck equation. This approach is equivalent to the master equation approach only for linear rate and transport laws.[24] For nonlinear systems the two approaches are equivalent only if a detailed description of all the higher moments of the stochastic source terms is known to fit the master equation. Both the master equation and the Fokker–Planck equation lead to the same qualitative consequences regarding the behavior of fluctuations near a critical point, though they differ somewhat in quantitative details.

In this section we shall consider the meaning of steady states and fluctuations from steady states using these two approaches for simple model systems. The linear approximation for a general system is considered in the next section.

A. Model systems

Consider a box which contains x particles, through which passes a flow of these particles (Fig. 8). The fluxes of particles into and out of the box depend on the number of particles in the box and on some external parameters $\lambda \equiv (\lambda_i)$. These fluxes are denoted by $Q(x, \lambda)$ and $R(x, \lambda)$, respectively. The macroscopic equation of motion is

$$dx/dt = Q(x, \lambda) - R(x, \lambda) \tag{IV.1}$$

and the corresponding steady state equation is

$$Q(x^0(\lambda), \lambda) = R(x^0(\lambda), \lambda) \ . \tag{IV.2}$$

The stochastic analog of this situation is a birth and death stochastic process. For simplicity we shall assume a Markoff process in which in each elementary step only one particle is added or eliminated, with rates $Q(x, \lambda)$ and $R(x, \lambda)$, respectively. If $P(x, \lambda, t)$ denotes the probability that the box contains x particles at time t under the constraints λ then the master equation is

$$\frac{\partial P(x,t)}{\partial t} = Q(x-1)\,P(x-1,t) + R(x+1)\,P(x+1,t) - (Q(x)+R(x))\,P(x,t) \ , \tag{IV.3}$$

where the dependence on λ was not written explicity. By expanding the first and second terms on the rhs of Eq. (IV.3) around x we obtain this equation in the form of an infinite order differential equation (the "Kramers Moyal expansion")

$$\frac{\partial P(x,t)}{\partial t} = \sum_{n=1}^{\infty} (-1)^n \left(\frac{\partial}{\partial x}\right)^n [M_n(x)\,P(x,t)] \ , \tag{IV.4}$$

where

$$M_n(x) = (1/n!)\,[Q(x) + (-1)^n R(x)] \ . \tag{IV.5}$$

This result is a special case of the general property of Markoff processes: Eq. (IV.4) always holds for such processes where however $M_n(x)$ is generally replaced by the nth moment of the transition probability

$$M_n(x,t) = \frac{1}{n!} \lim_{\Delta t \to 0} \frac{1}{\Delta t} \int dx'\, P(x', t+\Delta t \,|\, x, t)\,(x'-x)^n \tag{IV.6}$$

in which $P(x', t+\Delta t\,|\,x, t)$ is the conditional probability for the system to be in state x' at time $t+\Delta t$, given that it was in state x at time t.

A different stochastic model can be constructed from Eq. (IV.1) by adding a stochastic source term to its rhs, which leads to a Langevin equation

$$dx/dt = Q(x) - R(x) + A(x)\,g(t) \ . \tag{IV.7}$$

The Langevin function $g(t)$ obeys

$$\langle g(t) \rangle = 0 \tag{IV.8}$$

the average is taken over a long time or over a large ensemble of similar systems. The simplest choice for $g(t)$ is to assume that it is a Gaussian stochastic variable, that is we require

$$\langle g(t_1)\,g(t_2) \rangle = 2\delta(t_1 - t_2) \tag{IV.9a}$$

$$\left\langle \prod_{i=1}^{n} g(t_i) \right\rangle^L = 0; \quad n > 2 \ , \tag{IV.9b}$$

where $\langle\ \rangle^L$ denotes linked (or cumulant) averages. In calculating the moments of the transition probability [Eq. (IV.6)] for this process one obtains[23]

$$M_1(x) = G(x) + A(x)\,[dA(x)/dx] \ , \tag{IV.10}$$

$$M_2(x) = (A(x))^2 \ ,$$

$$M_n(x) = 0 \quad \text{for } n > 2 \quad , \tag{IV.11}$$

where

$$G(x) = Q(x) - R(x) \quad . \tag{IV.12}$$

With these results Eq. (IV.4) takes the form of a Fokker–Planck equation

$$\frac{\partial P(x,t)}{\partial t} = -\frac{\partial}{\partial x}[G(x)\,P(x,t)] + \frac{\partial}{\partial x}\left\{A(x)\frac{\partial}{\partial x}[A(x)\,P(x,t)]\right\} \quad . \tag{IV.13}$$

Note that from the general equation (IV.4) we obtain [by multiplying by x and integrating over all x, assuming that all the expressions involving $P(x,t)$ vanish at the limit of integration]

$$\partial\langle x\rangle/\partial t = \langle M_1(x)\rangle \quad . \tag{IV.14}$$

From Eq. (IV.11) it is evident that if we want to retain the kinetic equation of the form (IV.1) for $\langle x\rangle$, at least, we should take $A(x) \equiv K^{1/2} = \text{constant}$. This yields a Fokker–Planck equation of the form

$$\frac{\partial P}{\partial t} = -\frac{\partial}{\partial x}(GP) + K\frac{\partial^2}{\partial x^2}P \quad . \tag{IV.15}$$

The master equation and the Fokker–Planck equation approaches are now both characterized by the same first moment

$$M_1(x) = G(x) \tag{IV.16}$$

and by the same equation for the average

$$d\langle x\rangle/dt = \langle G(x)\rangle = \langle Q(x)\rangle - \langle R(x)\rangle \quad . \tag{IV.17}$$

They differ however in the equations of motion for the higher moments $\langle (x - \langle x\rangle)^n\rangle$. Physically Eq. (IV.3) seems more appropriate in case of chemical reactions whose stochastic description often takes the form of a birth and death process, while Eq. (IV.15) is suitable to describe a system whose stochastic nature is originated from an externally provided noise as may be the case for electrical circuits (or chemical systems with fluctuating environment).

In many works a master equation of a given stochastic process is used to derive a Fokker–Planck equation which hopefully describes approximately the same process. The primitive way to achieve this is to neglect higher than second order derivatives in Eq. (IV.4), assuming that the functions involved are sufficiently smooth.[25] This procedure has been shown by van Kampen[26] to be inconsistent; he suggested instead a systematic expansion of the master equation in inverse powers of $V^{1/2}$ or equivalently $N^{1/2}$ (V being the volume of the system and N the average number of particles). However, van Kampen's method is based on the assumption that fluctuations from the average are small relative to this average (more precisely $\Delta N/N \sim V^{-1/2}$). It cannot be used for our purpose, that is for exploring the amplitude of fluctuations near critical points. The master equation, Eq. (IV.3) should thus be solved without approximating it first by a Fokker–Planck equation.

In what follows we shall utilize both approaches, Eqs. (IV.3) and (IV.15) to study the properties of simple models of unstable systems. Such models are easily obtained by suitable choices of the functions $Q(x,\boldsymbol{\lambda})$ and $R(x,\boldsymbol{\lambda})$. Thus if we take

$$\begin{aligned} Q(x,\lambda,\mu) &= \mu x + \lambda \quad \mu, \lambda \geq 0 \\ R(x,\lambda,\mu) &= x^3 \end{aligned} \tag{IV.18}$$

then we have a system with the same "macroscopic" behavior (Eqs. (II.3) and (II.4) with a change of sign λ) studied in Sec. II, which was found to exhibit a first order (hard) transition. For the choice

$$\begin{aligned} Q(x,\lambda) &= \lambda x; \quad \lambda \geq 0 \\ R(x,\lambda) &= x^2 \end{aligned} \tag{IV.19}$$

we obtain a system [Eq. (II.37)] which macroscopically exhibits a second order transition. Note that both Eqs. (IV.18) and (IV.19) may correspond to chemical reactions in open systems (with reverse reactions neglected). Thus the rate laws in Eq. (IV.18) may originate from a system of chemical reactions

$$\begin{aligned} &A \rightarrow X \\ &B + X \rightarrow 2X \\ &3X \rightarrow 2X + C \end{aligned} \tag{IV.20}$$

in which A and B are kept constants, while the rates in Eq. (IV.19) correspond to

$$\begin{aligned} &A + X \rightarrow 2X \\ &2X \rightarrow X + B \end{aligned} \tag{IV.21}$$

where A is kept constant.

As was discussed in Sec. II the "macroscopic" equation of motion which corresponds to Eq. (IV.18) has one or three steady state solutions while the one corresponding to Eq. (IV.19) always has two steady states. Turning to the stochastic analogs, Eq. (IV.3) and (IV.15), we see a basic difference as these equations are known to possess a unique stable steady state solution for the distribution $P(x)$.[23d] However, the "macroscopic" steady states retain a meaning in the stochastic description since $P(x)$ has extremum values at these points, such that local maxima correspond to stable steady states and local minima to unstable steady states. To see this we note that the macroscopic steady states are the solutions $x^0(\lambda)$ of the equation

$$G(x_0,\lambda) = Q(x^0,\lambda) - R(x^0,\lambda) = 0 \tag{IV.22}$$

such that for stable steady states $(\partial G/\partial x)_{x^0} < 0$ and for unstable ones $(\partial G/\partial x)_{x^0} > 0$. Starting with Eq. (IV.15), we obtain its steady state solution from

$$G(x,\lambda)\,P_{st}(x,\lambda) = K\frac{\partial}{\partial x}P_{st}(x,\lambda) \quad , \tag{IV.23}$$

where P_{st} denotes the steady state distribution. We have assumed that the probability current $J = GP - K(\partial/\partial x)P$ vanishes at the boundaries (in x space) and, being constant at steady state, vanishes everywhere. From Eq. (IV.23) it is evident that $(\partial P/\partial x)_{st} = 0$ implies $G = 0$. Moreover, taking the derivative of Eq. (IV.23) with respect to x and using $\partial P_{st}/\partial x = 0$, then due to the fact that P_{st} is positive-definite, we see that $(\partial G/\partial x)_{x^0}$ and $(\partial^2 P/\partial x^2)_{st}$ have the same sign. This proves the relation be-

tween the stability of the macroscopic steady state and the nature of the extremum in P_{st}.[27]

Turning now to Eq. (IV.3), we can recast the steady state equation in the form

$$(e^{-\partial/\partial x} - 1)\,Q(x)\,P_{st}(x) = (1 - e^{\partial/\partial x})\,R(x)\,P_{st}(x)$$
$$= e^{\partial/\partial x}(e^{-\partial/\partial x} - 1)\,R(x)\,P_{st}(x) \qquad \text{(IV.24)}$$

which leads to[28]

$$Q(x)\,P_{st}(x) = R(x+1)\,P_{st}(x+1)$$

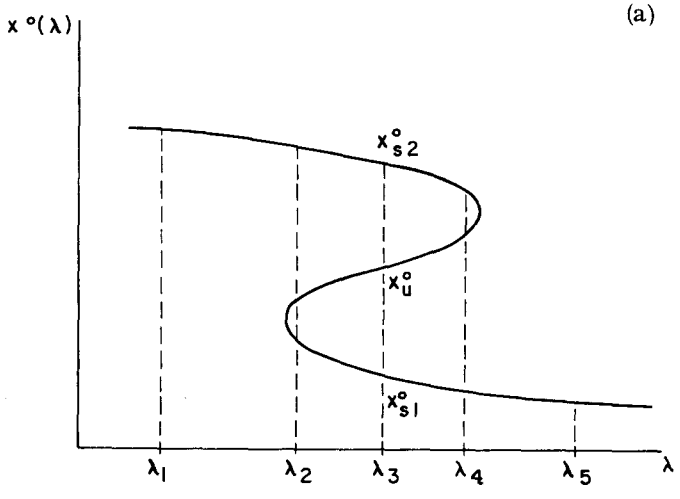
or

$$P_{st}(x+1) = [Q(x)/R(x+1)]\,P_{st}(x) \quad , \qquad \text{(IV.25)}$$

so that $P(x)$ is an increasing function of x when $Q(x) > R(x+1) = R(x)$ (the last equality holds when $x \gg 1$, that is for large systems), and is a decreasing function of x when the opposite inequality exists. An extremum of $P(x)$ occurs whenever $Q(x) = R(x+1) \simeq R(x)$ which is the macroscopic steady state equation. If $d(Q-R)/dx < 0$ this is clearly a maximum; otherwise it is a minimum.

For more general statements about the relation between macroscopic steady states and extreumum points of the distribution function see Appendix B.

The picture in which a unique stable steady state distribution exists, where different macroscopic stable steady states correspond to different maxima in this probability distribution, raises some doubts concerning the independent existence of steady states and the occurrence of hysteresis in hard transitions which are implied by the macroscopic equations of motion. Similar problems are encountered concerning the existence of a state of nonzero average magnetization in ferromagnets below the critical temperature, the existence of a state of nonzero average electric field in a laser above threshold and the existence of thermodynamic metastable states. The problem is demonstrated in Fig. 9, which schematically represents [Fig. 9(b)] the steady state distribution function $P_{st}(x, \lambda)$ for different values of a parameter λ, for a system in which the macroscopic steady state $x^0(\lambda)$ is



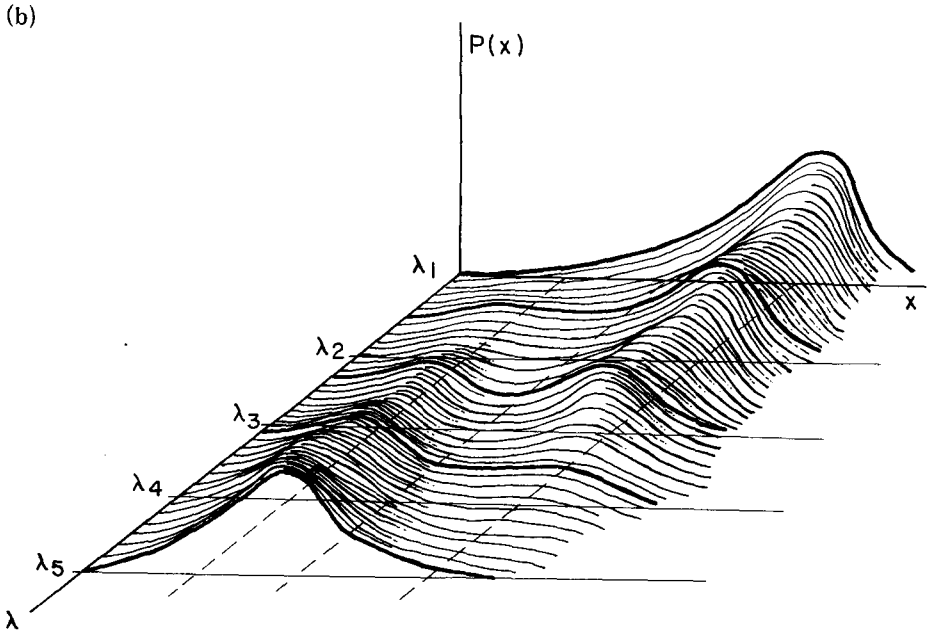


FIG. 9. Probability distribution for multistate system. (a) A diagram representing multiple steady states (compare with Fig. 2). (b) Probability distribution of the variable x for different values of the external parameter λ.

a multivalued function of λ [Fig. 9(a)]. The macroscopic description, Fig. 9(a) implies a hysteresis loop as was discussed in Sec. II, while the stochastic description [Fig. 9(b)] exhibits a gradual change in the steady state probability distribution.

This apparent paradox is resolved by considering the time scales involved when λ is changed. When we start from a steady state at $\lambda = \lambda_1$ (Fig. 9) and increase λ to the value $\lambda = \lambda_3$, then the system's relaxation to the new steady state distribution involves two time scales: a short time scale for the relaxation within the initial branch and a longer time scale for populating x values at the vicinity of the other macroscopic steady state, which for $\lambda = \lambda_3$ is equally probable according to the complete steady state distribution. If the rate of changing λ is fast relative to the long time scale of diffusion between different branches, but is slow relative to the relaxation rate within the initial branch, the "macroscopic" state of affairs will hold: the system will move along the initial (upper) branch until λ approaches λ_4. When the system begins from $\lambda = \lambda_5$ and λ is decreased with the same rate as before, the system will move along the original (lower) branch until λ approaches λ_2. According to this description hysteresis exists as long as the external parameter λ is changed on an appropriate time scale. It should be noticed however that when a marginal stability point (λ_4 or λ_2) is approached (from left or right respectively) the rate of relaxation within the initial branch decreases while the rate of transition from the initial to the other branch becomes faster (see below). When, for some value of λ, these two rates become comparable (which occurs before λ reaches its transition value) the original branch can no longer claim an independent existence on the time scale of the experiment. Macroscopically we expect the crossing point to occur (with some distribution) at the vicinity of this value of λ. We thus conclude that the marginal stability points are never realized (except of course for critical points).

To get a better feeling of the time scales involved in this description consider the Fokker Planck equation, Eq. (IV.15), with the model given by Eq. (IV.18), namely

$$\frac{\partial P}{\partial t} = -\frac{\partial}{\partial x}\left[(-x^3 + \mu x + \lambda)\, P\right] + K\frac{\partial^2 P}{\partial x^2} \quad . \tag{IV.26}$$

The unnormalized steady state solution of this equation is

$$P_{st}(x) = \exp\left[-\frac{1}{K}\left(\frac{1}{4}x^4 - \frac{\mu}{2}x^2 - \lambda x\right)\right] \quad , \tag{IV.27}$$

which has one or two maxima according to whether the macroscopic steady state equation $x^3 - \mu x - \lambda = 0$ has one or three real solutions. Consider the case of three macroscopic steady states and let $x^0_{s1} < x^0_{s2}$ denote the two stable ones and x^0_u—the unstable one. From the discussion of Sec. II we have $x^0_{s1} < x^0_u < x^0_{s2}$. Moreover, when marginal stability is approached x^0_u approaches x^0_{s1} (at the point λ_2 of Fig. 9) or x^0_{s2} (at the point λ_4).

To obtain the relaxation rate within a given stable steady state, x^0_{s1} say, it is sufficient to linearize Eq. (IV.26) for small deviations from this value of x. Putting $\xi = x^0_{s1}$ we get

$$\frac{\partial P(\xi, t)}{\partial t} = \frac{\partial}{\partial \xi}\left[\gamma_1\, \xi P\right] + K\frac{\partial^2 P(\xi)}{\partial \xi^2} \quad , \tag{IV.28}$$

where

$$\gamma_1 = 3(x^0_{s1})^2 - \mu$$

which leads to (c.f. Ref. 23a)

$$\langle \xi(t)\, \xi(0)\rangle = \exp(-\gamma_1 t)\, \langle \xi(0)\, \xi(0)\rangle \tag{IV.29}$$

for the time correlation function of fluctuations around the steady state considered (see Sec. V for a discussion of a multidimensional system). The relaxation time is determined by the external parameters μ and λ [which determine $x^0(\lambda, \mu)$]. At marginal stability of x^0_{s1} we have, according to Eq. (II.17a), $3x^0_{s1} - \mu = 0$, that is the relaxation time within the steady state becomes longer as marginal stability is approached.

The steady state distribution which corresponds to Eq. (IV.28) is a Gaussian centered around $\xi = 0$

$$P_{st} = \left(\frac{\gamma_1}{2\pi K}\right)^{1/2} \exp\left[-\frac{\gamma_1}{2K}(x - x^0_{s1})^2\right] \quad . \tag{IV.30}$$

The other stable steady state is disregarded by the linearization procedure which leads to Eq. (IV.28). To obtain an estimate of the time scale for diffusion between the two stable steady states, consider a system for which the initial distribution is given by Eq. (IV.30) but which evolves according to Eq. (IV.26). We integrate Eq. (IV.26) from x^0_u to ∞, assuming that P and its derivatives vanish at infinity at all times to get for

$$W(t) = \int_{x^0_u}^{\infty} P(x, t)\, dx$$

$$\frac{\partial W}{\partial t} = -K\left(\frac{\partial P}{\partial x}\right)_{x^0_u} \quad . \tag{IV.31}$$

Next, on using Eq. (IV.30) we get for the initial rate of populating the x^0_{s2} region

$$\frac{\partial W}{\partial t} = \left(\frac{\gamma_1^3}{2\pi K}\right)^{1/2} (x^0_u - x^0_{s1}) \exp\left(-\frac{\gamma_1}{2K}(x^0_u - x^0_{s1})^2\right) \quad . \tag{IV.32}$$

This clearly gives an upper bound for the rate of transition from x^0_{s1} to x^0_{s2}. When the distance $x^0_u - x^0_{s1}$ is large and if K is not too large, this rate is vanishingly small. When marginal stability is approached, $\partial W/\partial t$ increases (as both γ_1 and $x^0_u - x^0_{s1}$ go to zero). This rate takes a maximum value of $\gamma_1/(2\pi e)^{1/2}$ for $x^0_u - x^0_{s1} = (K/\gamma_1)^{1/2}$, but it should be kept in mind that this analysis cannot be carried too close to marginal stability because then the initial Gaussian distribution is meaningless.[29]

After establishing the relation between macroscopic steady states and the stochastic description of nonlinear systems we turn to consider the behavior of fluctuations from stable steady states when critical points are approached. Very little can be said about multidimensional systems without utilizing the linearization approximation.[30] We study fluctuations under this approximation in the following section. For future reference we consider here a simple example without using this approximation. As we noted above, theoretical transition points of hard transitions cannot be experimentally reached. Meaningful results can be obtained in case of hard transitions only for the approach to a critical point. In case

of second order (soft) transition marginal stability points are always identical to critical points and they are in principle always physically realizable. We therefore consider the system (IV.18) for the case $\lambda = 0$. When μ approaches zero this system approaches its critical point. Note that this system has been used in Sec. II to demonstrate both hard and soft transitions.

For this system, the Fokker–Planck equation [Eq. (IV.15)] yields the unnormalized distribution [Eq. (IV.27) with $\lambda = 0$]

$$P_{st}^{FP}(x) = \exp\left[-\frac{1}{2K}\left(\tfrac{1}{2}x^4 - \mu x^2\right)\right] \qquad \text{(IV.33)}$$

while, from the master equation approach we get, using Eq. (IV.25)

$$P_{st}^{M}(x) = P_{st}^{M}(1)\frac{\mu^{x-1}}{x(x!)^2} \quad \begin{matrix}\text{for } x > 0 \\ \text{and } \mu > 0\end{matrix} . \qquad \text{(IV.34)}$$

The distribution (IV.33) can be studied both above ($\mu > 0$) and below ($\mu < 0$) the critical point. An estimation of the noise around the macroscopic steady states is given by the function

$$N(\mu) = \left[\int_0^\infty P_{st}^{FP}(x)\,dx\right]^{-1} \int_0^\infty (x - \sqrt{\mu})^2 P_{st}^{FP}(x) \; ; \quad \mu > 0$$
$$= \left[\int_0^\infty P_{st}^{FP}(x)\,dx\right]^{-1} \int_0^\infty x^2 P_{st}^{FP}(x) \; ; \quad \mu < 0 . \qquad \text{(IV.35a)}$$

For $\mu < 0$, $N(\mu)$ is simply the amplitude, $\langle (x - x^0)^2 \rangle$, of fluctuation around the single steady state $x^0 = 0$. For $\mu > 0$, $N(\mu)$ gives an estimate of the fluctuations around the positive ($x^0 = \sqrt{\mu}$) stable steady state, which is meaningful only far enough from the critical point. The function $N(\mu)$ is plotted as a function of μ in Fig. 10(a).

The distribution (IV.34) is meaningful only for positive μ and x. The master equation (IV.3) with $Q(x) = \mu x$, $R(x) = x^3$ has a natural boundary at $x = 0$, and thus describes only fluctuations around the steady state $x = \sqrt{\mu} > 0$. The corresponding noise is given by

$$\langle (x - x^0)^2 \rangle = \left[\sum_{x=1}^{\infty} P_{st}^{M}(x)\right]^{-1} \sum_{x=1}^{\infty} (x - \sqrt{\mu})^2 P_{st}^{M}(x) \qquad \text{(IV.35b)}$$

and is plotted against $\mu > 0$ on Fig. 10(b). In both cases the noise is seen to increase when μ approaches its zero critical value.

V. FLUCTUATIONS IN GENERAL SYSTEMS IN THE LINEAR (GAUSSIAN) APPROXIMATION

In the last section we studied fluctuations in some simple model nonlinear systems and concluded that enhancement of fluctuations and lengthening of their decay time (critical slowing down) are to be expected when a system approaches marginal stability or a critical point. In this section we study the same phenomena for a general Markoffian system. The price we have to pay for this generality is that a linear approximation must be made. In this approximation the results obtained are: (a) Fluctuation amplitudes diverge at marginal stability or critical points. (b) The lifetime of fluctuations becomes infinite (or correlation times diverge) at the critical point. (c) Fluctuations become long range, i.e., the spatial correlation length diverges at the critical point. These conclusions result from the linear approximation and are not expected to be correct for the physical nonlinear system. Nevertheless, as we saw in the examples of Sec. IV (Fig. 10) the divergencies in the linear approximation reflect a finite growth of the corresponding quantities in the nonlinear case.

The results concerning the behavior of amplitude and lifetime of homogeneous fluctuations in the linear approximation may be found in the literature and are merely cited here.

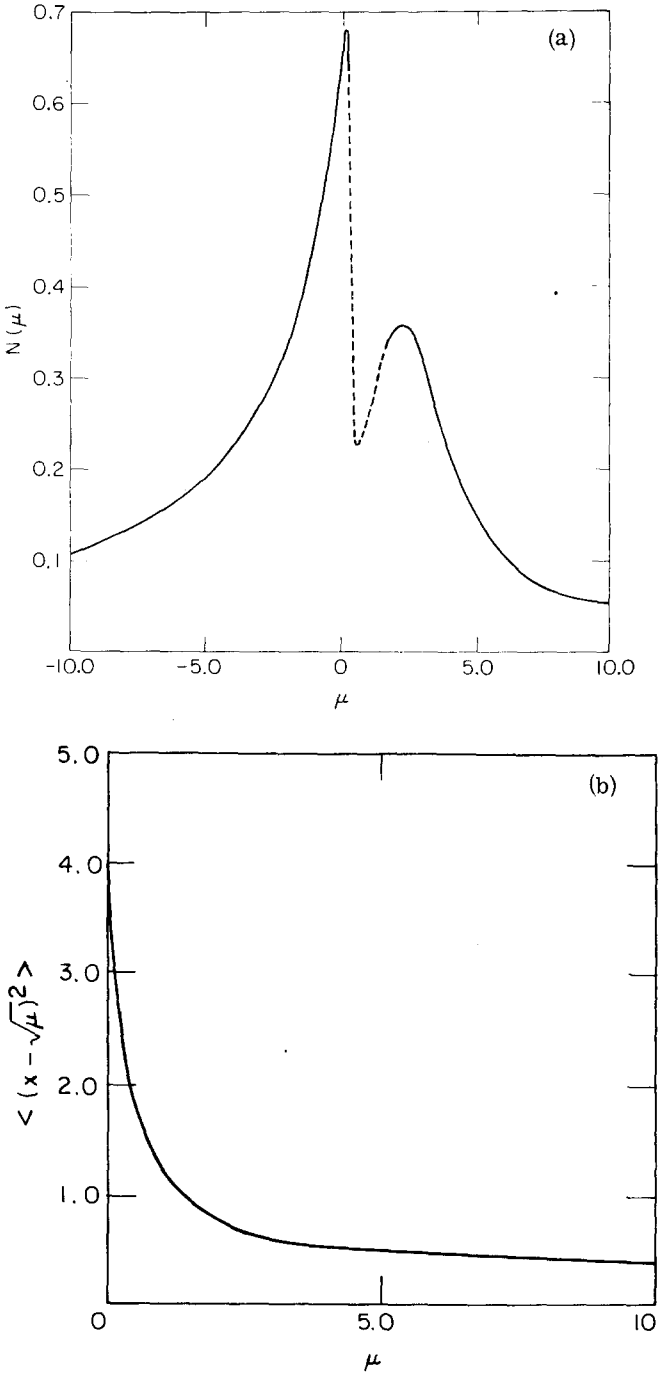


FIG. 10. The increase of noise near a critical point, given by $\mu = 0$. (a) A calculation based on Eq. (IV.35a). (b) A calculation based on Eq. (IV.35b). The results based on Eq. (IV.35a) are meaningless for small values of positive μ.

The correlation time is obtained from[23a]

$$\langle \delta\psi(t)\, \delta\psi(0)\rangle = \exp[+\Omega(\lambda)\, t]\, \langle \delta\psi\, \delta\psi\rangle \quad , \tag{V.1}$$

where

$$\delta\psi = \psi - \psi^0(\lambda) \tag{V.2}$$

and where, like in Secs. II and III ψ denotes the set of variables (like chemical concentrations) which determine the state of the system while λ is a set of external conditions. $\psi^0(\lambda)$ is the steady state of the system under the conditions λ. $\Omega(\lambda)$ is the linearized rate matrix defined in Eq. (III.6).[31] Finally, $\langle \delta\psi\, \delta\psi\rangle$ denotes the steady state equal time correlation function. As the real part of at least one of the roots of Ω vanishes at marginal stability or critical points, it follows that the lifetime of fluctuations diverge like $(\mathrm{Re} z_u)^{-1}$ (z_u being the unstable root).

The amplitude of fluctuations is obtained in the linear approximation from the relation

$$-2\mathbf{K}(\lambda) = \Omega(\lambda)\, \langle \delta\psi\, \delta\psi\rangle + \langle \delta\psi\, \delta\psi\rangle\, \Omega^{\dagger}(\lambda) \quad , \tag{V.3}$$

where $\Omega^{\dagger}$ is the transpose of Ω and where $\mathbf{K}$ is a constant "diffusion" matrix which is defined as the second moment of the transition probability [Eq. (IV.6) with x replaced by the vector ψ] evaluated at $\psi = \psi^0(\lambda)$. Mazo[36] has shown that the components of the matrix $\langle \delta\psi\, \delta\psi\rangle$ are inversely proportional to the quantity $\Pi_i \Pi_j (z_i(\lambda) + z_j(\lambda))$, where $(z_i(\lambda))$ are the eigenvalues of $\Omega(\lambda)$, and where i and j go over all these eigenvalues. It thus follows that the amplitude of fluctuations also diverges as $(\mathrm{Re} z_u)^{-1}$. Note that when several roots become unstable the fluctuations of the amplitude will diverge as $\Pi_u (\mathrm{Re} z_u)^{-1}$, that is faster than the correlation time.

In the rest of this section we study the behavior of the spatial correlation length. For this we make use of the Langevin approach,[23c] assuming that our system is adequately described by the set of kinetic equations

$$\frac{\partial \psi(r, t)}{\partial t} = \mathbf{D}\nabla^2 \overline{\psi}(r, t) + \mathbf{F}[\psi(\mathbf{r}, t), \lambda] + \mathbf{g}(r, t) \quad , \tag{V.4}$$

where $\mathbf{F}$ is again a set of nonlinear rate laws and $\mathbf{D}$ is a matrix of diffusion coefficients which is assumed to be constant on the time scale of the fluctuations considered and also to be independent of ψ. Finally $\mathbf{g}(r, t)$ is a stochastic Gaussian source[32]

$$\langle \mathbf{g}(\mathbf{r}, t)\rangle = 0 \tag{V.5a}$$

$$\langle \mathbf{g}(r_1 t_1)\, \mathbf{g}(r_2 t_2)\rangle = \mathbf{K}\delta(\mathbf{r}_1 - \mathbf{r}_2)\, \delta(t_1 - t_2) \quad , \tag{V.5b}$$

where $\mathbf{K}$ is a constant matrix. Let $\psi^0(\lambda)$ be a homogeneous steady state and suppose that $\mathbf{g}$ is small enough to justify consideration of small deviations $\delta\psi(r, t)$ from ψ^0. Then Eq. (V.4) can be replaced by the linear equation

$$\frac{\partial \delta\psi(r, t)}{\partial t} = \mathbf{D}\nabla^2\, \delta\psi(r, t) + \Omega(\lambda)\, \delta\psi(\mathbf{r}, t) + \mathbf{g}(\mathbf{r}, t) \quad . \tag{V.6}$$

Taking Fourier transforms in time and space of Eq. (V.6) such that

$$\delta\psi(k, \omega) = \frac{1}{(2\pi)^4} \int_{-\infty}^{\infty} e^{-ik\cdot r} e^{-i\omega t}\, \delta\psi(\mathbf{r}, t)\, dt d^3 r \tag{V.7}$$

and similarly for $\mathbf{g}(\mathbf{k}, \omega)$, we obtain

$$(i\omega + \Lambda)\, \delta\psi(\mathbf{k}, \omega) = \mathbf{g}(\mathbf{k}, \omega) \quad , \tag{V.8}$$

where

$$\Lambda = \Lambda(k, \lambda) = k^2\, \mathbf{D} - \Omega(\lambda) \tag{V.9}$$

and where a product of $i\omega$ with the unit matrix is implied. From Eq. (V.8) and its Hermitian conjugate we get

$$\langle \delta\psi(\mathbf{k}, \omega)\, \delta\psi(\mathbf{k}'\omega')\rangle = (i\omega + \Lambda)^{-1}\, \langle \mathbf{g}(k\omega)\, \mathbf{g}(k'\omega')\rangle\, (-i\omega' + \Lambda^{\dagger})^{-1} \quad . \tag{V.10}$$

Assuming that the system is invariant to time and space displacements so that

$$\langle \mathbf{g}(\mathbf{r}, t)\, \mathbf{g}(\mathbf{r}', t')\rangle = \langle \mathbf{g}(\mathbf{r} - \mathbf{r}',\ t - t')\, \mathbf{g}(0, 0)\rangle \quad , \tag{V.11}$$

Eq. (V.10) with Eq. (V.5b) allows us to write

$$\langle \delta\psi(\mathbf{r}, t)\, \delta\psi(0, 0)\rangle = \int_{-\infty}^{\infty} d^3\mathbf{k} d\omega e^{i\omega t + i\mathbf{k}\cdot\mathbf{r}} [i\omega + \Lambda]^{-1}\, \mathbf{K}[-i\omega + \Lambda^{\dagger}]^{-1} . \tag{V.12}$$

We evaluate first the integral over ω. To this end we observe that each term in the integrand matrix has the denominator $\det(i\omega + \Lambda)\det(-i\omega + \Lambda^{\dagger}) = |\det(i\omega + \Lambda)|^2$. Let $\eta_j(k, \lambda)$ ($j = 1.2\ldots$) be the eigenroots of $\Lambda(k, \lambda)$. This denominator is then

$$\prod_j (i\omega + \eta_j)\, (-i\omega + \eta_j^*) \tag{V.13}$$

which vanishes at $\omega = i\eta_j$, $-i\eta_j^*$. The real part of $\eta_j(k, \lambda)$ is positive (as our reference steady state is stable) so that only the poles $\omega = i\eta_j$ contribute to the ω integration with the result[33]

$$\langle \delta\psi(r, t)\, \delta\psi(0, 0)\rangle = 2\pi i \sum_j \mathbf{R}_j(\mathbf{r}, t) \quad , \tag{V.14}$$

where

$$R_j(\mathbf{r}, t) = \int d^3 k e^{i\mathbf{k}\cdot\mathbf{r}} e^{-\eta_j(k)t}\, \mathbf{S}_j(k) \tag{V.15}$$

with

$$\mathbf{S}_j(k) = \frac{\mathbf{B}_j(k)}{2\mathrm{Re}\eta_j(k)\, \Pi_{i\neq j}[-\eta_j(k) + \eta_i(k)]\, [\eta_j(k) + \eta_i^*(k)]} \quad . \tag{V.16}$$

$\mathbf{B}_j(k)$ in Eq. (V.16) is an analytic function of k. Noting that the integrand in Eq. (V.15) is a function of the scalar $k(= |\mathbf{k}|)$ only, we perform the angular integration and Eq. (V.15) can be replaced by

$$\mathbf{R}_j(\mathbf{r}, t) = \frac{1}{ir} \int_{-\infty}^{\infty} dk e^{ikr} e^{-\eta_j(k)t}\, k\mathbf{S}_j(k) \quad . \tag{V.17}$$

Consider first the simplest case of the equal time correlation function ($t = 0$) in Eqs. (V.14), (V.15), and (V.17) and diagonal difusion matrix with equal elements ($\mathbf{D} = D\mathbf{I}$ where I is the unit matrix). In this case

$$\eta_j(k, \lambda) = -z_j(\lambda) + k^2 D \quad , \tag{V.18}$$

where $z_j(\lambda)$ is the jth eigenvalue of $\Omega(\lambda)$ of which the real part is negative. Note that the restriction $\eta_j(k, \lambda) \neq \eta_i(k, \lambda)$ implies here that $\Omega(\lambda)$ is nondegenerate. For $t = 0$ we can perform the integral over k in Eq. (V.17) by complex integration. The terms in the denominator are

$$2\mathrm{Re}\eta_j(k, \lambda) = (k\sqrt{2D} + i\sqrt{2\,|\mathrm{Re} z_j(\lambda)|})(k\sqrt{2D} - i\sqrt{2\,|\mathrm{Re} z_j(\lambda)|}) \tag{V.19a}$$

$$-\eta_j(k,\boldsymbol{\lambda})+\eta_l(k,\boldsymbol{\lambda})=z_j(\boldsymbol{\lambda})-z_l(\boldsymbol{\lambda}) \tag{V.19b}$$

$$\eta_j(k,\boldsymbol{\lambda})+\eta_l^*(k,\boldsymbol{\lambda})=2k^2D-z_j(\boldsymbol{\lambda})-z_l^*(\boldsymbol{\lambda})$$
$$=(k\sqrt{2D}+a_{jl}+ib_{jl})(k\sqrt{2D}-a_{jl}-ib_{jl}) \ , \tag{V.19c}$$

where, in Eq. (V.19c), a_{jl} abd b_{jl} are real numbers, defined by this equation. Using these expressions we rewrite $\mathbf{R}_j(\mathbf{r},0)$ as

$$\mathbf{R}_j(\mathbf{r},0)=\frac{1}{ir}\left(\mathbf{A}_{jj}\exp\left[-\sqrt{\frac{\mathrm{Re}z_j(\lambda)}{D}}\,r\right]\right.$$
$$\left.+\sum_l \mathbf{A}_{jl}\exp\left[i\frac{a_{jl}}{\sqrt{2D}}r-\frac{b_{jl}}{\sqrt{2D}}r\right]\right) , \tag{V.20}$$

where $\mathbf{A}_{jl}$ is a constant matrix which is unimportant for our purpose. Let the index u denote the roots $z_u(\boldsymbol{\lambda})$ for which the real part vanishes at $\boldsymbol{\lambda}=\boldsymbol{\lambda}_c$ (a critical or marginal stability point). The correlation function $\langle\psi(r,0)\times\psi(0,0)\rangle$, Eq. (V.14), can be written in the form

$$\langle\psi(\mathbf{r},0)\,\psi(0,0)\rangle=\frac{2\pi}{r}\sum_u \mathbf{A}_{uu}\exp\left[-\sqrt{\frac{\mathrm{Re}z_u(\lambda)}{D}}\,r\right]$$
$$+\frac{2\pi}{r}\times(\text{terms which decay exponentially in } r). \tag{V.21}$$

When $\boldsymbol{\lambda}$ approaches $\boldsymbol{\lambda}_c$ the second term in Eq. (V.21) can be neglected for large r. It is seen that the correlation length diverges as $[\mathrm{Re}z_u(\lambda)]^{-1/2}$. This result is in agreement with those obtained for the spatial correlation length at the threshold of the Benard instability in liquids.[8,9] It should also be compared with the similar result obtained for the divergence of the penetration length of perturbations applied at the boundary of an unstable system [Eq. (III.23)].

Note that $a_{jl}\neq 0$ for some j and l only if $\boldsymbol{\Omega}$ has some roots for which the imaginary part is nonzero. From Eq. (V.20) it follows that such roots are always associated with oscillations in the correlation function.

Next, consider the case $t\neq 0$, where still $\mathbf{D}=D\mathbf{I}$. From Eq. (V.15) we have

$$\mathbf{R}_j(\mathbf{r},t)=e^{z_j(\lambda)t}\rho_j(\mathbf{r},t) \ , \tag{V.22}$$

where

$$\rho_j(\mathbf{r},t)=\int d^3k e^{i\mathbf{k}\cdot\mathbf{r}}e^{-k^2Dt}\mathbf{S}_j(k) \ . \tag{V.23}$$

Note that ρ satisfies a diffusion equation

$$\frac{\partial\rho}{\partial t}=\frac{1}{D}\nabla^2\rho \tag{V.24}$$

which could be solved with the result (V.20) as the initial condition. Rather than pursuing this possibility we note that if only long time behavior is desired, the integral (V.23) can be evaluated approximately. When t is very large, only small values of k contribute to the integral and approximately[34]

$$\rho_j(\mathbf{r},t)=\mathbf{S}_j(k=0)\int d^3k e^{i\mathbf{k}\cdot\mathbf{r}}e^{-k^2Dt}$$
$$=\mathbf{S}_j(k=0)\,e^{-r^2/4Dt}\,(2\pi/Dt)^{3/2} \ . \tag{V.25}$$

The time correlation function thus decays at long times like $(1/t^{3/2})e^{z_j(\lambda)t}$. The slow $t^{-3/2}$ decay becomes significant for the term $\mathbf{R}_u$ when the critical point is approached.

Finally, consider the equal time correlation function ($t=0$) for a general diffusion matrix $\mathbf{D}$. Here again we have to find the poles of $\mathbf{S}_j(k)$, Eq. (V.16). If κ is such a pole the corresponding contribution to the space correlation function behaves like

$$(1/r)\exp[i\,\mathrm{Re}\kappa r-\mathrm{Im}\kappa r] \ . \tag{V.26}$$

The poles κ are functions of the external parameters $\boldsymbol{\lambda}$. At marginal stability ($\lambda=0$) there is a root $\eta_u(k)$ for which $\mathrm{Re}\eta_u(k)=0$ for some real (not necessarily zero) k. That means that $\mathbf{S}_u(k)$ has a pole $\kappa(\boldsymbol{\lambda})$ whose imaginary part becomes zero at marginal stability. This corresponds according to (V.26) to an infinite spatial correlation length. If, during the process of changing $\boldsymbol{\lambda}$, $\mathrm{Re}\eta_u(k)$ becomes zero first at zero k, then not only $\mathrm{Im}\kappa$ but also $\mathrm{Re}\kappa$ are zero at marginal stability, and the slowly decaying contribution to the correlation function, (V.26), has no structure. This is the case for $\mathbf{D}=\mathbf{I}D$. For a general $\mathbf{D}$ it may happen that $\mathrm{Re}\eta_u(k)$ vanishes first for a given nonzero k (symmetry breaking instabilities). In (V.26) that means that $\mathrm{Im}\kappa$ becomes zero at marginal stability while $\mathrm{Re}\kappa$ remains different from zero. The corresponding contribution to the correlation function is then structured and oscillates like $\exp(i\cdot\mathrm{Re}\kappa\cdot r)$. We thus conclude that symmetry breaking instabilities correspond to oscillating spatial correlation functions.

VI. CONCLUDING REMARK

This paper has been devoted to an examination of the analogy between transitions in far from equilibrium reacting systems and phase transitions and critical phenomena. Our treatment, particularly in Sec. V, closely resembles the Landau–Ginzburg theory[16,35] and accordingly we obtain "classical" results for the exponents characterizing the points of marginal stability. For example in three dimensions [see Eq. (V.21)]

$$\mathbf{G}(\mathbf{r})=\langle\psi(\mathbf{r},0)\,\psi(0,0)\rangle\sim\mathbf{A}r^{-1}\exp[-r\xi] \ ,$$

where ξ^{-1} is a correlation length. It is important to note that by "classical" exponents we do not necessarily mean Landau–Ginzburg exponents which correspond to a particular nonlinear model [i.e., the critical point of Eq. (II.27)]. Thus the most general prediction about the divergence of ξ^{-1} is that it diverges like $(\lambda-\lambda_c)^{\delta}$, where $\delta\geq 1/4$ [see discussion following Eq. (III.33)]. In the model (II.27) one obtains $\delta=\frac{1}{2}$ which is the Landau–Ginzburg exponent, but cases where $\delta=\frac{1}{4}$ are quite common.

Recent advances in the theory of critical phenomena due to the renormalization group approach[37–39] may have an immediate application to the problems of chemically unstable systems. Since in many complex chemical systems the number of components n of the state vector of concentration variables ψ is likely to be large, the renormalization group expansion in powers of $(1/n)$ (where n is the dimension of the internal "spin" variable)[39,40] may well prove most useful. More important from the chemical point of view is the recent extension of the renormalization group techniques by Halperin, Hohenberg, and Ma[41] to dynamical critical phenomena. These work-

ers begin with an assumed set of kinetic equations of a structure very similar to that displayed in Eq. (V.4) and apply renormalization group arguments to investigate critical slowing down. We are presently investigating the application of these ideas to the problems in chemical instabilities.

APPENDIX A

Here we apply the formalism of Sec. II to obtain marginal stability and critical points in a system characterized by the kinetic equation

$$\begin{aligned} dA/dt &= -(k_1 + k_2)A + k_2 a \\ dT/dt &= \alpha A - \beta(T - T_e) - h(dA/dt) \quad . \end{aligned} \tag{A1}$$

with $k_i = \kappa_i e^{-R_i/T} (i = 1, 2)$, where $\kappa_{1,2}$, $R_{1,2}$, a, β, and h are constants; T_e and α are externally determined parameters. These kinetic equations determine the behavior of a chemically reactive (A B) illuminated system with temperature dependent rate coefficients.[42] In reduced quantities

$$\begin{aligned} &x = T\beta/\alpha a \; ; \quad \lambda = T_e \beta/\alpha a \; ; \quad \mu = (R_2 - R_1)(\beta/\alpha a) \\ &k = \kappa_2/\kappa_1 \end{aligned} \tag{A2}$$

the steady state equation takes the form

$$G(x, \lambda, \mu) \equiv x - [\kappa \exp(\mu/x) + 1]^{-1} - \lambda = 0 \quad . \tag{A3}$$

Equation (A3) has been shown[42] to have one or three (two stable one unstable) solutions. Transitions between the stable steady states are of the first order. We can now use Eqs. (II.10) and (II.11b) to obtain the following equations for the marginal stability lines in the $(\lambda\mu x)$ space.

$$\begin{aligned} &[1 - (x - \lambda)]/(x - \lambda) = \kappa e^{\mu/x} \\ &(\kappa e^{\mu/x} + 1)^2 = (\kappa \mu/x^2) e^{\mu/x} \quad . \end{aligned} \tag{A4}$$

These are two equations in three variables, which define a line (or lines) in the $(\lambda\mu x)$ space. To obtain the critical point we note first that for the G defined by Eq. (A3) the condition (II.11) implies that the two relations (II.12a) and (II.12b) are equivalent and thus correspond to the same critical point. The condition for the critical point is obtained from Eq. (II.14)

$$[(2/x) + (\mu/x^2)](1 + \kappa e^{\mu/x}) = 2 \tag{A5}$$

which must hold simultaneously with (A4). These three conditions for the three variables λ, μ, x define a point in the $(\lambda\mu x)$ space.

APPENDIX B

Here we generalize the relation discussed in Sec. IV between macroscopic steady states and extremum points of the steady state distribution function. The general one dimensional master equation may be written in the form

$$\frac{dP(x)}{dt} = \sum_r (e^{-n(r)(\partial/\partial x)} - 1) Q_r(x) P(x) \quad , \tag{B1}$$

where r denotes a given reaction and $n(r)$ is the number of particles created $[n(r) > 0]$ or eliminated $[n(r) < 0]$ in the process r. The sum is over all the rate processes which characterize the system. Now let $m = n$ for $n > 0$ and $l = -n$ for $n < 0$. At steady state we can write

$$\begin{aligned} \sum_m (e^{-m(\partial/\partial x)} - 1) Q_m(x) P_{st}(x) &= -\sum_l (e^{l(\partial/\partial x)} - 1) Q_{-l}(x) P_{st}(x) \\ &= \sum_l (e^{-l(\partial/\partial x)} - 1) e^{l(\partial/\partial x)} Q_{-l}(x) P_{st}(x) \quad . \end{aligned} \tag{B2}$$

Using

$$\begin{aligned} e^{-k(\partial/\partial x)} - 1 = (e^{-\partial/\partial x} - 1)(1 + e^{-\partial/\partial x} + e^{-2(\partial/\partial x)} + \ldots \\ + e^{-(k-1)(\partial/\partial x)}) \end{aligned} \tag{B3}$$

and cancelling the operator $e^{-\partial/\partial x} - 1$ on both sides[28] we have

$$\begin{aligned} &\sum_m (1 + e^{-\partial/\partial x} + e^{-2(\partial/\partial x)} + \ldots e^{-(m-1)(\partial/\partial x)}) Q_m(x) P_{st}(x) \\ &= \sum_l (e^{l(\partial/\partial x)} + e^{(l-1)(\partial/\partial x)} + \ldots + e^{(\partial/\partial x)}) Q_{-l}(x) P_{st}(x) \quad . \end{aligned} \tag{B4}$$

This is a difference equation of high order which involves the probability distribution at points $x - m + 1$, $\ldots, x, \ldots, x + l$ for all the values of l and m involved. Let x_0 be an extremum point of $P_{st}(x)$. In the vicinity of x_0, $P_{st}(x)$ is a slowly varying function of x and, if $\max(l)$ and $\max(m)$ are not too large we can replace $P_{st}(x)$ by a constant in all the terms of Eq. (B4), so that

$$\begin{aligned} &\sum_m (1 + \ldots + e^{-(m-1)(\partial/\partial x)}) Q_m(x) \\ &= \sum_l (e^{l(\partial/\partial x)} + \ldots + e^{(\partial/\partial x)}) Q_l(x) \end{aligned} \tag{B5}$$

where both sides are evaluated at $x = x_0$. For large systems $(x_0 \gg 1)$ all the exponent operators may be expanded and only their zero order term retained, such that

$$\sum_m m Q_m(x_0) = \sum_l l Q_{-l}(x_0) \tag{B6}$$

which is the steady state equation.

In the multidimensional case we have

$$\sum_{\mathbf{n}} (e^{-\mathbf{n}\cdot\partial/\partial \mathbf{x}} - 1) Q_{\mathbf{n}}(\mathbf{x}) P_{st}(\mathbf{x}) = 0 \quad , \tag{B7}$$

where now $\mathbf{n}$ is the index of a process in which n_i particles of component i are created if $n_i > 0$, or destroyed if $n_i < 0$, with the rate $Q_n(x)$. The method used in the one dimensional case seems here intractable unless we have a detailed balance condition (i.e., at equilibrium)

$$e^{-\mathbf{n}(\partial/\partial \mathbf{x})} Q_{\mathbf{n}}(\mathbf{x}) P_{st}(\mathbf{x}) - Q_{-\mathbf{n}}(\mathbf{x}) P_{st}(\mathbf{x}) = 0 \tag{B8}$$

for every $\mathbf{n}$. This leads to

$$P_{st}(x) = \frac{Q_{\mathbf{n}}(\mathbf{x} - \mathbf{n})}{Q_{-\mathbf{n}}(\mathbf{x})} P_{st}(\mathbf{x} - \mathbf{n}) \tag{B9}$$

for every $\mathbf{n}$, which shows that $P(x)$ has its extremum when $Q_{\mathbf{n}}(\mathbf{x}) = Q_{-\mathbf{n}}(\mathbf{x})$ for every $\mathbf{n}$. From the LeChatelier principle it immediately follows that this extremum is a maximum.

When detailed balance does not exist we can still study the multidimensional case assuming that Van Kampen's approach[26] is applicable. Again let $\mathbf{x}_0$ be a maximum point of $P_{st}(\mathbf{x})$ and assume that the distribution around $\mathbf{x}_0$ is such that

$$\mathbf{x} = V(\mathbf{y}_0 + V^{-1/2}\mathbf{y}) \quad , \tag{B10}$$

where V is a size parameter of the system (e.g., its volume), and where $\mathbf{y}_0 = \mathbf{x}_0/V$. Also assume that the rate laws are such that

$$Q_n(\mathbf{x}) = Vq_n(\mathbf{y}_0 + V^{-1/2}\mathbf{y}) \tag{B11}$$

where q_n as well as $\mathbf{y}_0$ and $\mathbf{y}$ are $O(1)$. Then Eq. (B7) can be expanded in powers of $V^{-1/2}$ in exactly the same way that this was done by Van Kampen for the one dimensional case, giving

$$0 = \sum_{m=1}^{\infty}\sum_{l=1}^{m}(-1)^l V^{-1/2m}\frac{1}{l!(m-l)!} \times\left(\frac{\partial}{\partial \mathbf{y}}\right)^l : \left\{\left[\sum_n (\mathbf{n})^l\left(\frac{\partial a_n(\mathbf{y}_0)}{\partial \mathbf{y}_0}\right)^{m-l} : (\mathbf{y})^{m-l}\right]\pi(\mathbf{y})\right\} , \tag{B12}$$

where $\pi(\mathbf{y}) = P(\mathbf{x}) = P(\mathbf{x}_0 + V^{1/2}\mathbf{y})$ and where

$$(\mathbf{a})^k : (\mathbf{b})^k = \sum_{i_1}\sum_{i_2}\cdots\sum_{i_k} a_{i_1}a_{i_2}\cdots a_{i_k}b_{i_1}b_{i_2}\cdots b_{i_k} .$$

The term $m=1$ $l=1$ [which is $(V^{-1/2})$] then gives

$$\frac{\partial \pi(\mathbf{y})}{\partial \mathbf{y}}\cdot\sum_n \mathbf{n}q_n(\mathbf{y}_0) = 0 \tag{B13}$$

for every $\mathbf{y}$ in the domain of applicability of Eq. (B12). As $\partial\pi/\partial\mathbf{y}$ is in general different from zero this leads to

$$\sum_n \mathbf{n}q_n(\mathbf{y}_0) = \sum_n \mathbf{n}Q_n(\mathbf{x}_0) = 0 \tag{B14}$$

which is the steady state equation.

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