Chemical instabilities as critical phenomena*

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The analogy between equilibrium phase transitions and chemical instabilities is studied in detail in the vicinity of the critical point of a nonequilibrium reacting diffusing system characterized by multiple homogeneous steady states. The critical point of such a system is defined and its mathematical properties are discussed. These properties are shown to be essential in the subsequent reduction of the equations of motion near the critical point. The order parameter characterizing the transition is defined, and its equation of motion near the critical point is obtained in the form of a time-dependent Ginzburg-Landau equation. Fluctuations are taken into account phenomenologically using a Langevin-equation approach. Fluctuations originating from diffusion processes are shown not to be important near the critical point. The size of the critical region for chemical instabilities is estimated using an equivalent of the Ginzburg criterion of equilibrium critical phenomena. The reduction method fails within this region. It is concluded that critical points of chemical instabilities can in principle exhibit "nonclassical" critical behavior. Systems involving the photothermochemical instability and computer simulations of model systems seem currently to be the best candidates for studying the critical properties of chemical instabilities, and for experimental or numerical tests of the predictions of the present theory.

I. INTRODUCTION

Instabilities and transition phenomena in nonequilibrium systems have been in recent years subject to extensive research effort. Much attention has been particularly given to universal features characterizing different phenomena of this kind and to their close analogy to equilibrium phase transitions.[1] Laser transitions,[2] hydrodynamical instability,[3] and chemical instabilities[4,5] are some of the most common examples that were studied in analogy to equilibrium phase transitions and critical phenomena. It has been pointed out[2-5] that enhancement of fluctuations, long-range order, and critical slowing down are typical to nonequilibrium transition phenomena in much the same way as they characterize equilibrium critical points. In macroscopic nonequilibrium systems where stochastic dynamical equations of motion are the starting points of most theoretical considerations, these features of the nonequilibrium critical behavior can all be traced to the existence of slow mode (or modes) near the transition point. If τ is the lifetime of the soft mode, the amplitude of fluctuations is of the order τ^{-1} (in the linear approximation[6]), while $\sqrt{\tau D}$ (D is a typical diffusion coefficient) is a characteristic length which becomes large near the critical point.

Unlike most equilibrium phase transitions, nonequilibrium transitions often give rise to states which are structured in space, in time or in both space and time (traveling structures). For such temporal and spatial symmetry-breaking transitions the mathematical analogy to equilibrium critical phenomena has recently been demonstrated.[1c,1d,3c,3d,5] In particular, it was pointed out that the amplitude of the (spatially or temporally) ordered mode plays the role of an order parameter for the nonequilibrium transitions. This order parameter was shown to satisfy, near the nonequilibrium critical point, an equation of motion similar to the time-dependent Ginzburg-Landau (TDGL) equation which is used to describe critical dynamics near equilibrium.

In this paper we focus attention on transitions in chemical systems characterized by multiple homogeneous steady states. Such transitions are usually induced by the homogeneous mode which becomes soft as the transition point is approached. Transitions of this type are expected to be the most closely related to equilibrium phase transitions which usually take place between homogeneous stationary states. Typical examples are given by the Schlogl model[4a]

$$A + x \rightleftarrows 2x, \quad B + x \rightarrow C$$

in which the concentration of A, B, and C are kept constant and play the role of externally controlled parameters,[7] and by the Edelstein model described in Sec. V. The main motivation for the interest in this type of nonequilibrium transition is the recent experiment by Creel and Ross[8] who, following a suggestion by Nitzan and Ross,[9] demonstrated the occurrence of multiple steady states in a photothermochemical system. In the particular experiment performed,[8] the reaction $2NO_2 \rightleftarrows N_2O_4 + (\text{heat})$ is taken away from equilibrium in a closed system by illumination with a high-intensity light beam of a wavelength which is absorbed by the NO_2 only. The system is characterized by

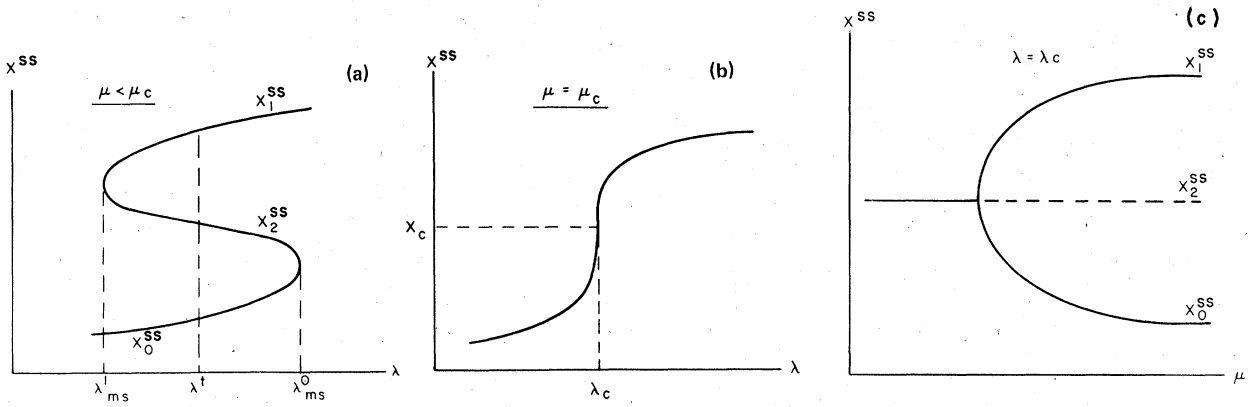

FIG. 1. Schematic description of multiple steady states and the approach to the critical point. (a) Situation with three steady states x_0^{ss}, x_1^{ss}, and x_2^{ss} which may coexist in a given range of λ. λ_{ms} are marginal stability points and λ_t is the value of λ for which the branches x_1 and x_0 are equally stable. (b) The approach to the critical point as λ is varied for $\mu=\mu_c$. (c) The approach to the critical point as μ is varied for $\lambda=\lambda_c$.

two-state variables, (the concentration of NO_2 and the temperature say)[10] and by two externally controlled parameters (external temperature and incident light intensity).[11] Far enough from equilibrium the system may appear in two stable steady states; one with large NO_2 concentration and high temperature and the other in which the NO_2 concentration and the temperature are both low. The transition between these states is induced by the homogeneous mode. Unlike many other nonequilibrium chemical systems, this system is relatively easily controlled and it should be possible to study its critical properties.

Figure 1 displays a typical situation with three steady states in a system characterized by two external parameters μ and λ. In the usual situation shown in Fig. 1(a) we expect to observe a hysteresis loop when a state variable x is monitored as a function of λ. The marginally stable points corresponding to λ_{ms}^0 and λ_{ms}^1 can never be realized because finite amplitude fluctuations will cause a transition from the less-stable to the more-stable branch before these points are reached. In fact, if λ is changed infinitely slowly we expect the transition to occur at a well-defined point λ_t, and the hysteresis loop shrinks to zero. This situation is quite analogous to equilibrium phase transitions where λ_t corresponds to the Maxwell construction on the van der Waals equation, and where the extensions beyond it correspond to metastable branches. For a particular value, $\mu = \mu_c$, of the other controlled parameter, the three steady states coalesce at a critical point $x=x_c$, $\lambda=\lambda_c$ [Fig. 1(b)]. This point is in principle attainable within an uncertainty distance which depends on our ability to control λ and μ. The situation in which λ is fixed at its critical value $\lambda=\lambda_c$ and μ is changed is shown in Fig. 1(c).

To study critical properties of such a nonequilibrium system we have to focus on the vicinity of the critical point $\lambda=\lambda_c$, $\mu=\mu_c$. From the theoretical point of view the following questions come to mind: (i) What is the order parameter characterizing this transition? (ii) What is the equation of motion for this order parameter? (iii) How do fluctuations affect the critical behavior? (iv) What is the limit of validity of a mean-field theory and can we expect "nonclassical" critical exponents? In this paper we discuss and partly answer these questions for the case of nonequilibrium systems characterized by homogeneous steady states. We rely on methods developed before[3d, 3e, 5, 12] for symmetry breaking transitions which we modify to admit also the treatment of homogeneous transitions. It will be seen that this approach fails in the immediate vicinity of the critical point but we argue that it is sufficient to give a reliable estimate of the critical region.

In Sec. II we investigate the mathematical properties of marginal stability and critical points which correspond to homogeneous transitions. In Sec. III we perform the reduction of the kinetic equations and obtain an equation of motion for the order parameter. We show in this section that this reduction is possible only provided that the critical conditions obtained in Sec. II are satisfied. In Sec. IV we discuss fluctuations and in Sec. V we work out a particular simple example in detail. Finally, in Sec. VI we obtain and discuss the Ginzburg estimate for the size of the critical region in diffusing reacting chemical systems.

II. PROPERTIES OF MARGINALLY STABLE AND OF CRITICAL POINTS

We begin by considering a system characterized by a set of deterministic dynamic equations of the

form

$$\frac{d\vec{x}}{dt} = \vec{D} \cdot \nabla^2 \vec{x} + \vec{F}(\vec{x}, \vec{\lambda}), \tag{2.1}$$

which is typical to a reacting-diffusing multicomponent system. The variables $\vec{x}(\vec{r}, t)$ define the state of the system at any given time, while the parameters $\vec{\lambda}$ are externally controlled. The diffusion matrix $\vec{D}$ is assumed to be constant. As mentioned before, we limit ourselves to systems where transitions to instabilities occur via homogeneous nonoscillatory modes. Such transitions usually occur between multiple homogeneous steady states.

In what follows we consider explicitly only a single externally controlled parameter λ which is changed in order to approach a marginally stable or a critical point. The set of equations

$$\vec{F}(\vec{x}, \lambda) = 0, \tag{2.2}$$

characterizing a steady state of the system, will be called equations of state. Let $\vec{x}_0(\lambda)$ be a solution of this set for a given λ. We introduce the derivative matrix[13]

$$\vec{\Omega}(\vec{x}, \lambda) = \partial \vec{F}(\vec{x}, \lambda)/\partial \vec{x}. \tag{2.3}$$

We also define the associated Jacobian

$$J(\vec{x}, \lambda) = \det[\vec{\Omega}(\vec{x}, \lambda)] \tag{2.4}$$

and the corresponding steady-state matrix and determinant

$$\vec{\Omega}_0(\lambda) = \vec{\Omega}[\vec{x}_0(\lambda), \lambda], \tag{2.5}$$

$$J_0(\lambda) = \det[\vec{\Omega}_0(\lambda)]. \tag{2.6}$$

The partial derivatives appearing above are all taken with λ kept constant. In addition, it will be convenient to define derivatives taken along the steady-state line of the $(n+1)$-dimensional $(\vec{x}, \lambda)$ space. Along this line λ, or any one of the $x_1 \cdots x_n$ variables, can be taken as an independent variable. Such derivatives will always be written as total (d/dx) derivatives, with specifications of variables which are kept constant added if necessary to avoid confusion.

For a stable steady state all the roots of $\vec{\Omega}_0(\lambda)$ are negative. At a marginally stable point at least one of the roots of $\vec{\Omega}_0$ vanishes, while the rest are still negative. Equivalently,

$$J_0(\lambda_{ms}) = 0, \tag{2.7}$$

where λ_{ms} denotes the value of λ at the marginally stable point. As was discussed before,[4b] such points are characterized by a divergence of the "response functions" $dx_{0j}(\lambda)/d\lambda$ or, equivalently,

$$\lim_{\lambda \to \lambda_{ms}} \frac{d\lambda}{dx_{0j}} \to 0, \quad j = 1, 2, \ldots, n. \tag{2.8}$$

To see the equivalence between conditions (2.7) and (2.8) we consider one of the equations of states, e.g.,

$$F_1(\vec{x}, \lambda) = 0, \tag{2.9}$$

and take its derivative with respect to one of the variables, e.g., x_1, keeping all conditions for steady state, $F_j = 0, j = 2, \ldots, n$ holding. This is just

$$\left(\frac{dF}{dx_1}\right)_{F_2 \cdots F_n} = \left(\frac{\partial F_1}{\partial x_1}\right)_{F_2 \cdots F_n; \lambda} + \left(\frac{\partial F_1}{\partial \lambda}\right)_{F_2 \cdots F_n; x_1} \frac{d\lambda}{dx_1}. \tag{2.10}$$

This is a derivative along the steady-state line so that the left-hand side (2.10) vanishes. Also, at a marginally stable point, $d\lambda/dx_1 = 0$. Hence

$$(\partial F_1/\partial x_1)_{F_2 \cdots F_n; \lambda} = 0 \quad \text{(marginal stability)}. \tag{2.11}$$

Using some known identities from the calculus of Jacobians it is easy to show (Appendix A)

$$(\partial F_1/\partial x_1)_{F_2 \cdots F_n; \lambda} = J/J_1, \tag{2.12}$$

where

$$J_1 = \partial(F_2 \cdots F_n)/\partial(x_2 \cdots x_n). \tag{2.13}$$

In the derivatives entering into J and J_1, λ is kept constant. We have thus proved that, provided $J_1 \neq 0$, the conditions $J = 0$ and $d\lambda/dx_1 = 0$ are equivalent.[14a] $J_1 \neq 0$ generally holds unless the first row component of the null eigenvector of the matrix $\vec{\Omega}_0(\lambda_{ms})$ vanishes (see Appendix B).

We turn now to the definition and properties of critical points. In analogy to the Landau-Ginzburg theory we define a critical point as a point on the steady-state line satisfying

$$d\lambda/dx_j = d^2\lambda/dx_j^2 = 0 \tag{2.14}$$

for at least one x_j[14b] and in addition to the steady-state condition $\vec{F}(\vec{x}, \lambda) = 0$. We now wish to recast this condition in a form which does not involve the explicit dependence of λ on x_j. To this end we start again from Eq. (2.10) and take its derivative with respect to x_1. We note that all contributions arising from the second term on the right-hand side of (2.10) are proportional to either $d\lambda/dx$, or to $d^2\lambda/dx^2$, and therefore vanish at the critical point if Eq. (2.14) holds for $j = 1$. We thus find

$$(\partial^2 F_1/\partial x_1^2)_{F_2 \cdots F_n; \lambda} = 0 \quad \text{(critical point)}. \tag{2.15}$$

Equation (2.15) should hold at the critical point, together with the equations of state $\vec{F} = 0$ and the marginally stability condition $J = 0$. Together we have $n+2$ conditions for the $n+1$ $(\vec{x}, \lambda)$ variables. Obviously, another external parameter besides λ shoud be adjusted appropriately to insure the existence of a critical point. Equation (2.15) may be recast in the form

$$[(\partial/\partial x_1)(J/J_1)]_{F_2\cdots F_n;\lambda}=0 \quad \text{(critical point)}. \tag{2.16}$$

Equation (2.16), together with the conditions $J=0$, $J_1\neq 0$, yield

$$(\partial J/\partial x_1)_{F_2\cdots F_n;\lambda}=0 \quad \text{(critical point)}. \tag{2.17}$$

In Appendix A we show that Eq. (2.17) is equivalent to the equation

$$\partial(J, F_2\cdots F_n)/\partial(x_1, x_2\cdots x_n)=0 \quad \text{(critical point)}. \tag{2.18}$$

Obviously, x_1 and F_1 have no special standing in our arguments and an equation equivalent to (2.18) is easily shown to hold for any variable for which Eq. (2.14) is satisfied, together with the requirement $J_j(\lambda_c)\neq 0$. (λ_c is the critical value of λ.)

It will prove useful for our future purpose to express the condition (2.18) in another form. We start by expanding the rate vector $\vec{F}(\vec{x}, \lambda_c)$ around the critical point $\vec{x}_c$ which we choose here as our origin for $\vec{x}(\vec{x}_c=0)$,

$$\vec{F}(\vec{x}, \lambda_c)=\vec{\Omega}_c\vec{x}+\vec{G}(\vec{x}), \tag{2.19}$$

where $\vec{\Omega}_c=\vec{\Omega}(\vec{x}_c, \lambda_c)$ and where $\vec{G}(\vec{x})$ contains all the terms which are nonlinear in $\vec{x}$. The determinant J now takes the form

$$J=\det(\vec{\Omega}_c+\partial\vec{G}/\partial\vec{x}) \quad \text{for } \lambda=\lambda_c. \tag{2.20}$$

The condition (2.18) involves derivatives of J with respect to $x_1, x_2\cdots x_n$ at $\vec{x}=\vec{x}_c=0$ and at $\lambda=\lambda_c$. The only terms in J which may contribute to such derivatives are those linear in $\partial\vec{G}/\partial\vec{x}$. We may thus replace J in Eq. (2.18) by

$$J\to\frac{\partial\vec{G}}{\partial\vec{x}}:\vec{C}=\sum_{ij}\frac{\partial G_i}{\partial x_j}C_{ij}, \tag{2.21}$$

where C_{ij} is the cofactor of Ω_{ij} in $\vec{\Omega}$. Equation (2.18) then takes the form

$$\begin{vmatrix} \left[\frac{\partial}{\partial x_1}\left(\frac{\partial\vec{G}}{\partial\vec{x}}:\vec{C}\right)\right]_c & \left[\frac{\partial}{\partial x_2}\left(\frac{\partial\vec{G}}{\partial\vec{x}}:\vec{C}\right)\right]_c \cdots & \left[\frac{\partial}{\partial x_n}\left(\frac{\partial\vec{G}}{\partial\vec{x}}:\vec{C}\right)\right]_c \\ (\Omega_c)_{21} & (\Omega_c)_{22}\cdots(\Omega_c)_{2n} & \\ \vdots & \vdots\quad\vdots & \\ (\Omega_c)_{n1} & (\Omega_c)_{n2}\cdots(\Omega_c)_{nn} & \end{vmatrix}=0. \tag{2.22}$$

The subscripts (c) indicate that all quantities are to be calculated at the critical point. Expanding the determinant in the first row we obtain

$$\sum_{i=1}^{n} C_{1i}\frac{\partial}{\partial x_i}\left(\frac{\partial\vec{G}}{\partial\vec{x}}:\vec{C}\right)=0 \quad \text{(critical point)}. \tag{2.23}$$

Equation (2.23) may be recast in still another form. Define the right and left eigenvectors of $\vec{\Omega}_c$ which correspond to the vanishing eigenvalues, in the form

$$\vec{\Omega}_c\cdot\vec{u}_0=0, \quad \vec{\tilde{\Omega}}_c\cdot\vec{u}_0^{(1)}=0. \tag{2.24}$$

($\vec{\tilde{\Omega}}$ is the transpose of $\vec{\Omega}$); then Eq. (2.23) is shown in Appendix C to be equivalent to[15]

$$\vec{u}_0^{(1)}\cdot\left(\frac{\partial^2\vec{G}}{\partial\vec{x}\partial\vec{x}}:\vec{u}_0\vec{u}_0\right)=0 \quad \text{(critical point)} \tag{2.25}$$

where the left-hand side should be interpreted as

$$\sum_{ijk}(u_0^{(1)})_i\left(\frac{\partial^2 G_i}{\partial x_j\partial x_k}\right)(u_0)_j(u_0)_k.$$

In summary, a critical point of a system characterized by a set of dynamic equations of the kind (2.1) and having transitions between homogeneous steady states is defined as a steady-state point satisfying Eq. (2.14), and was shown to satisfy also Eqs. (2.7) and (2.18). Equation (2.18) was shown to be equivalent to Eq. (2.23) and to Eq. (2.25).

III. REDUCTION OF THE EQUATIONS OF MOTION

In this section we utilize the methods of reductive perturbation theory in order to extract an equation of motion for the order parameter describing the transition. This equation is valid near the critical point and is obtained by focusing on the slow-time and long-distance scale which characterize the motion of the order parameter.

The method is based on the multiple time and space scales perturbation expansion of the equations of motion. It has been extensively used in analyzing bifurcation phenomena in various nonlinear systems. In particular, it has been applied in studying symmetry breaking transitions in hydrodynamics,[3d,3e] in lasers[1d] and in diffusing reacting chemical systems.[6] In the chemical case it was contended[6a] that the method is not appropriate for analyzing transitions without either temporal or spatial symmetry breaking, but as we shall show, the expansion can be performed in a self-consistent way provided the critical conditions are

satisfied.

For the time being we disregard fluctuations and we take as our starting point the deterministic equations of motion (2.1). In a later section we shall introduce fluctuations in a way similar to Graham's approach to the convection instability[3d] and to the laser transition.[1d]

Our expansion parameter is denoted ϵ and is defined as the order of deviation from the critical point,

$$\lambda = \lambda_c + \epsilon^2 \delta\lambda. \tag{3.1}$$

ϵ does not appear at the end of the calculation and $\delta\lambda$ will be retained as the measure of the physical distance from the critical point. It is assumed that the choice of λ was made such that the root of $\vec{\vec{\Omega}}_0(\lambda)$ which vanishes for $\lambda = \lambda_c$ is proportional to $\delta\lambda$. Next, we follow previous works[3d,5] in assuming that near the critical point the time and length scale characterizing the order parameter are of order ϵ^{-2} and ϵ^{-1}, respectively. As we are interested in the case where the transition involves a homogeneous nonoscillatory mode, it is possible to disregard the fast-time and short-length scale. We thus put

$$\partial/\partial t \to \epsilon^2(\partial/\partial\tau), \quad \nabla_r \to \epsilon \nabla_R. \tag{3.2}$$

Finally, the deviation of the state variable vector $\vec{\mathbf{x}}$ from the steady-state value $x_0(\lambda)$ is expanded in the form

$$\vec{\mathbf{x}} - \vec{\mathbf{x}}_0(\lambda) = \sum_{l=1}^{\infty} \epsilon^l \mathbf{x}_l. \tag{3.3}$$

Some comments on these choices of scaling are made in Appendix E. Note that we have chosen as our variable the deviation $\vec{\mathbf{x}} - \vec{\mathbf{x}}_0(\lambda)$ of the state vector from its steady-state value for given λ. An alternative way is to choose $\vec{\mathbf{x}} - \vec{\mathbf{x}}_c$—the deviation of the state vector from its critical value. As $\vec{\mathbf{x}}_0(\lambda) - \vec{\mathbf{x}}_c$ is itself of order ϵ (cf. Appendix E) the first term in both expansions is of order ϵ.

It is sometimes assumed that the matrix $\vec{\vec{\Omega}}_0(\lambda)$ can be expanded near the critical point in the form

$$\vec{\vec{\Omega}}_0(\lambda) = \vec{\vec{\Omega}}_c + \left(\frac{d\vec{\vec{\Omega}}_0}{d\lambda}\right)_c \delta\lambda. \tag{3.4}$$

This assumption which is usually valid for symmetry-breaking transitions does not generally hold for homogeneous transitions within our expansion scheme. To see this we note that $\vec{\vec{\Omega}}_0(\lambda) = \vec{\vec{\Omega}}[x_0(\lambda), \lambda]$ where $\vec{\vec{\Omega}}(\vec{\mathbf{x}}, \lambda) \equiv \partial\vec{\mathbf{F}}/\partial\vec{\mathbf{x}}$, $\vec{\mathbf{x}}_0(\lambda)$ being the solution to the equations of state $\vec{\mathbf{F}}(\vec{\mathbf{x}}, \lambda) = 0$ for a given λ. Thus,

$$\frac{d\vec{\vec{\Omega}}_0(\lambda)}{d\lambda} = \left(\frac{\partial\vec{\vec{\Omega}}}{\partial\vec{\mathbf{x}}}\right)_{\vec{\mathbf{x}}_0(\lambda)} \cdot \frac{\partial\vec{\mathbf{x}}_0(\lambda)}{\partial\lambda} + \frac{\partial\vec{\vec{\Omega}}_0(\lambda)}{\partial\lambda}, \tag{3.5}$$

and since $\vec{\mathbf{x}}_0(\lambda)$ is a nonanalytical function of λ near marginal stability or critical points, the expansion (3.4) will not be valid. In most chemically relevant cases (involving bimolecular reaction steps) $\vec{\vec{\Omega}}(x, \lambda)$ contain terms linear in components of $\vec{\mathbf{x}}$ so that the leading term in the expansion of $\vec{\vec{\Omega}}_0$ around $\vec{\vec{\Omega}}_c$ will be of order $O(\sqrt{\delta\lambda})$. A more explicit form of this term will be useful to us in our future manipulations. Near the critical point we have, to order ϵ,

$$\Omega_0(\lambda) = \vec{\vec{\Omega}}[x_0(\lambda), \lambda] = \vec{\vec{\Omega}}_c + \left(\frac{\partial\vec{\vec{\Omega}}(x, \lambda)}{\partial\vec{\mathbf{x}}}\right)_c [\vec{\mathbf{x}}_0(\lambda) - \vec{\mathbf{x}}_c]. \tag{3.6}$$

Actually, to this order, (cf. Appendix E)

$$\vec{\mathbf{x}}_0(\lambda) - \vec{\mathbf{x}}_c = \alpha_0 \vec{\mathbf{u}}_0, \quad \alpha_0 \sim O(\epsilon), \tag{3.7}$$

so that

$$\vec{\vec{\Omega}}_0(\lambda) - \vec{\vec{\Omega}}_c = \alpha_0 \left(\frac{\partial^2\vec{\mathbf{F}}}{\partial\vec{\mathbf{x}}\partial\vec{\mathbf{x}}}\right)_c \vec{\mathbf{u}}_0 \equiv \epsilon\sqrt{\delta\lambda}\,\vec{\vec{\Omega}}_1, \tag{3.8}$$

where we use the expansion

$$\alpha_0 = \epsilon\sqrt{\delta\lambda}\, a_1 + \epsilon^2 \delta\lambda a_2 + \cdots \tag{3.9}$$

and define

$$\vec{\vec{\Omega}}_1 \equiv a_1 \left(\frac{\partial^2\vec{\mathbf{F}}}{\partial\vec{\mathbf{x}}\partial\vec{\mathbf{x}}}\right)_c \cdot \vec{\mathbf{u}}_0 = a_1 \left(\frac{\partial^2\vec{\mathbf{G}}}{\partial\vec{\mathbf{x}}\partial\vec{\mathbf{x}}}\right)_c \cdot \vec{\mathbf{u}}_0. \tag{3.10}$$

Contributions of order ϵ^2 to $\vec{\vec{\Omega}}_0(\lambda) - \vec{\vec{\Omega}}_c$ may originate from three terms: First, $O(\epsilon^2)$ contributions to $\vec{\mathbf{x}}^0(\lambda) - \vec{\mathbf{x}}_c$ give

$$\sum_{j=1} \alpha_j \left(\frac{\partial\vec{\vec{\Omega}}}{\partial\vec{\mathbf{x}}}\right)_c \cdot \vec{\mathbf{u}}_j + \epsilon^2 \delta\lambda a_2 \left(\frac{\partial\vec{\vec{\Omega}}}{\partial\vec{\mathbf{x}}}\right)_c \cdot \vec{\mathbf{u}}_0, \tag{3.11}$$

(from Appendix E, $\alpha_j \sim O(\epsilon^2)$ for $j \neq 0$); second, $O(\alpha_0^2)$ contributions to the second-order term[15]

$$\left(\frac{\partial^2\vec{\vec{\Omega}}}{\partial\vec{\mathbf{x}}\partial\vec{\mathbf{x}}}\right)_c [\vec{\mathbf{x}}_0(\lambda) - \vec{\mathbf{x}}_c][\vec{\mathbf{x}}_0(\lambda) - \vec{\mathbf{x}}_c] \to \epsilon^2 \delta\lambda a_1^2 \left(\frac{\partial^2\vec{\vec{\Omega}}}{\partial\vec{\mathbf{x}}\partial\vec{\mathbf{x}}}\right)_c : \vec{\mathbf{u}}_0\vec{\mathbf{u}}_0; \tag{3.12}$$

Finally, when $\vec{\vec{\Omega}}$ depends explicitly on λ we have the term

$$\epsilon^2 (\partial\vec{\vec{\Omega}}/\partial\lambda)_c \delta\lambda. \tag{3.13}$$

In our following calculations we denote the sum of these three terms by $\epsilon^2\delta\lambda\vec{\vec{\Omega}}_2$, where $\vec{\vec{\Omega}}_2$ stands for the sum of matrices. We note that using expressions (3.11)–(3.13) we may write an explicit expression for $\vec{\vec{\Omega}}_2$ for any particular case.

Turning now to the nonlinear term $\vec{\mathbf{G}}(\vec{\mathbf{x}})$, we expand it in the form

$$\vec{\mathbf{G}}(\vec{\mathbf{x}}) = \frac{1}{2}\left(\frac{\partial^2\vec{\mathbf{G}}}{\partial\vec{\mathbf{x}}\partial\vec{\mathbf{x}}}\right)_0 [\vec{\mathbf{x}} - \vec{\mathbf{x}}_0(\lambda)][\vec{\mathbf{x}} - \vec{\mathbf{x}}_0(\lambda)] + \frac{1}{6}\left(\frac{\partial^2\vec{\mathbf{G}}}{\partial\vec{\mathbf{x}}\partial\vec{\mathbf{x}}\partial\vec{\mathbf{x}}}\right)_0 [\vec{\mathbf{x}} - \vec{\mathbf{x}}_0(\lambda)][\vec{\mathbf{x}} - \vec{\mathbf{x}}_0(\lambda)] \times [\vec{\mathbf{x}} - \vec{\mathbf{x}}_0(\lambda)] + \cdots. \tag{3.14}$$

The index 0 denotes evaluation at the steady-state point. To $O(\epsilon^2)$ only the first term in this expansion contributes. Also, if there are higher than quadratic nonlinearities in the expressions for the rates we have, to order ϵ,

$$\left(\frac{\partial^2\vec{G}}{\partial\vec{x}\partial\vec{x}}\right)_0=\left(\frac{\partial^2\vec{G}}{\partial\vec{x}\partial\vec{x}}\right)_c+\left(\frac{\partial^2\vec{G}}{\partial\vec{x}\partial\vec{x}\partial\vec{x}}\right)_c[\vec{x}_0(\lambda)-\vec{x}_c]-\left(\frac{\partial^2\vec{G}}{\partial\vec{x}\partial\vec{x}}\right)_c+\epsilon\sqrt{\delta\lambda}\,a_1\left(\frac{\partial^2\vec{G}}{\partial\vec{x}\partial\vec{x}\partial\vec{x}}\right)_c\cdot\vec{u}_0. \tag{3.15}$$

The second term on the right-hand side of Eq. (3.15) contributes only in $O(\epsilon^2)$. Equation (3.14) is thus seen to be equivalent (to order ϵ^3) to

$$\vec{G}(\vec{x})=\frac{1}{2}\left(\frac{\partial^2\vec{G}}{\partial\vec{x}\partial\vec{x}}\right)_c[\vec{x}-\vec{x}_0(\lambda)][\vec{x}-\vec{x}_0(\lambda)]+\frac{1}{6}\left(\frac{\partial^2 G}{\partial\vec{x}\partial\vec{x}\partial\vec{x}}\right)_c[x-x_0(\lambda)][x-x_0(\lambda)]\times\{[x-x_0(\gamma)]+3\epsilon\sqrt{\delta\lambda}\,a_1\vec{u}_0\}. \tag{3.16}$$

We now proceed in our program of reducing the equations of motion. In terms of our scaled variables these read

$$[-\vec{\Omega}_c-\epsilon\sqrt{\delta\lambda}\,\Omega_1+\epsilon^2(\partial/\partial\tau-\vec{D}\nabla_R^2-\delta\lambda\vec{\Omega}_2)]\vec{x}=\vec{G}(\vec{x}), \tag{3.17}$$

where here $\vec{x}$ denotes the deviation from the steady state and is given by the expansion (3.3). We now insert this expansion into Eq. (3.17) and consider it order by order.

First order. To order ϵ we obtain

$$\vec{\Omega}_c\cdot\vec{x}_1=0, \tag{3.18}$$

which implies

$$\vec{x}_1=W(\vec{R},\tau)\vec{u}_0. \tag{3.19}$$

$W(\vec{R},\tau)$ will be identified as the order parameter for this problem. It varies near the critical point on the long time and length scales. We require its equation of motion on these scales.

Second order. To order ϵ^2, Eq. (3.17) yields[15]

$$-\vec{\Omega}_c\vec{x}_2-\sqrt{\delta\lambda}\,\vec{\Omega}_1\vec{x}_1=\frac{1}{2}\left(\frac{\partial^2\vec{G}}{\partial\vec{x}\partial\vec{x}}\right)_c:\vec{x}_1\vec{x}_1. \tag{3.20}$$

The integrability condition for this equation,

$$-\sqrt{\delta\lambda}\,\vec{u}_0^{(1)}\cdot\vec{\Omega}_1\cdot\vec{x}_1=\tfrac{1}{2}\vec{u}_0^{(1)}\cdot\left[\left(\frac{\partial^2\vec{G}}{\partial\vec{x}\partial\vec{x}}\right)_c:\vec{x}_1\vec{x}_1\right], \tag{3.21}$$

is automatically satisfied near the critical point. Both sides vanish as may be realized from Eqs. (3.19), (3.10), and (2.25). The solution $\vec{x}_2$ is obtained in the form

$$\vec{x}_2=-[aW(\vec{R},\tau)+\tfrac{1}{2}W^2(\vec{R},\tau)]\vec{\Omega}_c^{-1}\cdot\left(\frac{\partial^2\vec{G}}{\partial\vec{x}\partial\vec{x}}\right)_c:\vec{u}_0\vec{u}_0,\qquad a\equiv a_1\sqrt{\delta\lambda}, \tag{3.22}$$

where Eqs. (3.19) and (3.10) were used again and where a_1 was defined by Eq. (3.9) and is an $O(1)$ parameter.

Denoting

$$\vec{v}\equiv\left(\frac{\partial^2\vec{G}}{\partial\vec{x}\partial\vec{x}}\right)_c:\vec{u}_0\vec{u}_0\equiv\sum_j\beta_j\vec{u}_j, \tag{3.23}$$

Eq. (3.22) may be recast in the form

$$\vec{x}_2=-(aW+\tfrac{1}{2}W^2)\sum_{j=1}^{n-1}\frac{\beta_j}{\gamma_j}\vec{u}_j. \tag{3.24}$$

We note in passing that $\vec{u}_0^{(1)}\cdot\vec{x}_2=0$.

Third order. In this order, we obtain

$$-\vec{\Omega}_c\cdot\vec{x}_3-\sqrt{\delta\lambda}\,\vec{\Omega}_1\cdot\vec{x}_2+\left(\frac{\partial}{\partial\tau}-\vec{D}\nabla_R^2-\delta\lambda\vec{\Omega}_2\right)\cdot\vec{x}_1=\left(\frac{\partial^2\vec{G}}{\partial\vec{x}\partial\vec{x}}\right)_c:\vec{x}_1\vec{x}_2+\left(\frac{\partial^3\vec{G}}{\partial\vec{x}\partial\vec{x}\partial\vec{x}}\right)_c\vdots\left(\frac{1}{6}\vec{x}_1\vec{x}_1\vec{x}_1+\tfrac{1}{2}a\vec{u}_0\vec{x}_1\vec{x}_1\right). \tag{3.25}$$

Note that from (3.10) it follows that $(\partial^2G/\partial\vec{x}\partial\vec{x})_c\vec{x}_1\vec{x}_2=(1/a_1)W\Omega_1\vec{x}_2$. Denoting

$$\begin{aligned}&\vec{u}_0^{(1)}\cdot\vec{\Omega}_2\cdot\vec{u}_0\equiv A_1,\\ &-\vec{u}_0^{(1)}\cdot\vec{\Omega}_1\cdot\vec{\Omega}_c^{-1}\cdot\vec{v}\equiv A_2,\\ &\vec{u}_0^{(1)}\cdot\left[\left(\frac{\partial\vec{G}}{\partial\vec{x}\partial\vec{x}\partial\vec{x}}\right)\vdots\vec{u}_0\vec{u}_0\vec{u}_0\right]\equiv A_3,\\ &\vec{u}_0^{(1)}\cdot\vec{D}\cdot\vec{u}_0\equiv\bar{D}.\end{aligned} \tag{3.26}$$

We obtain, from the integrability condition for Eq. (3.25), the following equation of motion for the order parameter W,

$$(\partial/\partial\tau-\bar{D}\nabla_R^2)W=(A_1+a_1A_2)\delta\lambda W+\tfrac{1}{2}(3A_2+a_1A_3)\sqrt{\delta\lambda}\,W^2+(A_2/2a_1+A_3/6)W^3. \tag{3.27}$$

This is an equation of the Ginzburg-Landau type. The absence of a W-independent term in this equation from choice of $\vec{x}_0(\lambda)$ as the origin for the state vector. Details of the calculations with some discussion of possible intricacies are provided for a particular example in Sec. V.

We have thus completed our task of formally extracting an equation of motion for the order parameter W. In this equation (3.27), $\delta\lambda$ measures the distance from the critical point.[26] We note that all the physical quantities characterizing the state of the system (components of the vector $\vec{x}$) are given near the critical point (to order ϵ) in terms of W by Eq. (3.19). Next we turn to considering fluctuations and their effect on the behavior of the system near the critical point.

IV. FLUCTUATIONS

In this section we consider the effect of internal fluctuations on the reduced equation of motion for the order parameter. We follow Graham[3d] in introducing fluctuations as Langevin-type fluctuating terms in the original equations of motion (2.1). We also follow his reasoning for obtaining the effect of these stochastic terms on the reduced equation.

Introducing fluctuations phenomenologically as Langevin terms added to nonlinear dynamic equations is presently a matter of some debate.[16,17] It seems to be generally agreed that far enough from critical and marginally stable points this procedure is valid. In this case, a Gaussian approximation for the probability distribution of the dynamic variables holds. Our main concern in analyzing the effects of fluctuations on the critical behavior will be to estimate the region near the critical point where this approximation breaks down. The answer to such a question can be given by approaching from the direction in which the Gaussian approximation (or equivalently mean-field theory) holds, in much the same way as the size of the critical region is estimated in theories of equilibrium critical phenomena.[18] A Langevin-type approach is therefore valid for this purpose. Also, since we are interested in rough estimates rather than in exact numbers, it is enough to use an order of magnitude estimate for the random terms which we add to the equations of motion. We therefore follow the procedure used in statistical hydrodynamic theories[19] and approximate the correlation functions of the random terms by their equilibrium values.[20] Such Langevin terms for chemically reacting multicomponent fluids near equilibrium have been recently provided by Grossmann.[21a] For our system where the only transport processes are reaction and diffusion, we have

$$\partial \mathbf{x}/\partial\tau = \vec{\mathbf{D}}\cdot\nabla^2\vec{\mathbf{x}} + \vec{\mathbf{F}}(\vec{\mathbf{x}}) + \vec{\mathbf{f}}, \tag{4.1}$$

where the Langevin terms $\vec{\mathbf{f}}$ may be written as sums of diffusion originated and of reaction originated terms. These are Gaussian stochastic variables with zero mean and with correlation functions given by

$$\langle f_j(\vec{\mathbf{r}},t) f_{j'}(\vec{\mathbf{r}}',t')\rangle = \sum_{\kappa} \langle f_j(\vec{\mathbf{r}},t) f_{j'}(\vec{\mathbf{r}}'t')\rangle^{(\kappa)} + \langle f_j(\vec{\mathbf{r}},t) f_{j'}(\vec{\mathbf{r}}'t')\rangle^{(D)}; \tag{4.2}$$

the index κ goes over all the chemical reactions involved in the system. The D term stands for the contribution of the diffusion processes. If we assume for simplicity that the diffusion matrix $\vec{\mathbf{D}}$ is diagonal and that the systems behave as an ideal fluid mixture, we obtain[21]

$$\langle f_j(\vec{\mathbf{r}},t) f_{j'}(\vec{\mathbf{r}}',t')\rangle^{(D)} = \frac{2D_j}{A_0}\delta_{jj'}\nabla_r[x_j(\vec{\mathbf{r}})\nabla_{r'}\delta(\vec{\mathbf{r}}-\vec{\mathbf{r}}')]\delta(t-t') \tag{4.3}$$

and

$$\langle f_j(\vec{\mathbf{r}},t) f_{j'}(\vec{\mathbf{r}}',t')\rangle^{(\kappa)} = \nu_{j\kappa}\nu_{j'\kappa} M_j M_{j'} \frac{\vec{\mathbf{r}}_\kappa + \overleftarrow{\mathbf{r}}_\kappa}{A_0}\delta(\vec{\mathbf{r}}-\vec{\mathbf{r}}')\delta(t-t'), \tag{4.4}$$

where D_j is the diffusion coefficient j, A_0 is the Avogadro number, $\nu_{j\kappa}$ is the stochiometric coefficient of component j in the reaction κ, M_j is the molecular weight of component j, and $\vec{\mathbf{r}}_\kappa, \overleftarrow{\mathbf{r}}_\kappa$ are rates of the reaction κ in the forward and backward directions, respectively. In writing Eqs. (4.3) and (4.4) we allowed for nonequilibrium situations in making it possible that $\vec{\mathbf{r}}_\kappa \neq \overleftarrow{\mathbf{r}}_\kappa$ and that x_j is space dependent. These generalized forms are obtained if we start with a master equation and go over to a Fokker-Planck (and the equivalent Langevin) equation in the conventional way involving a truncated Kramers-Moyal expansion.[17] We note that in writing Eqs. (4.3) and (4.4) we have taken $\{x_i\}$ to be concentrations measured in mass/unit volume. The reaction r_κ are measured in moles/unit volume/unit time.

Assuming for simplicity that x_j is $\vec{\mathbf{r}}$ independent and denoting

$$S_j = 2D_j x_j/A_0 \tag{4.5}$$

and

$$Q_{jj'} = \sum_{\kappa} \nu_{j\kappa}\nu_{j'\kappa}\frac{M_j M_{j'}}{A_0}(\vec{\mathbf{r}}_\kappa + \overleftarrow{\mathbf{r}}_\kappa), \tag{4.6}$$

we obtain

$$\langle f_j(\vec{\mathbf{r}},t) f_{j'}(\vec{\mathbf{r}}',t')\rangle = Q_{jj'}\delta(\vec{\mathbf{r}}-\vec{\mathbf{r}}')\delta(t-t') + \delta_{jj'} S_j \nabla_r\cdot\nabla_{r'}\delta(\vec{\mathbf{r}}-\vec{\mathbf{r}}')\delta(t-t'). \tag{4.7}$$

With the choice (3.2) for scaling Eq. (4.7) takes the form

$$\langle f_j(\vec{\mathbf{R}},\tau) f_{j'}(\vec{\mathbf{R}}',\tau')\rangle = \epsilon^{d+2} Q_{jj'}\delta(\vec{\mathbf{R}}-\vec{\mathbf{R}}')\delta(\tau-\tau') + \epsilon^{d+4}\delta_{jj'} S_j \nabla_{\mathbf{R}}\nabla_{\mathbf{R}'}\delta(\vec{\mathbf{R}}-\vec{\mathbf{R}}')\delta(\tau-\tau'), \tag{4.8}$$

where d denotes the dimensionality of the system. This form for the correlation function suggests that close enough to the critical point ($\epsilon \to 0$) the diffusion-originated contribution to the random force is negligible relative to the reaction-originated one. This makes physical sense: We focus on variations of long wavelength and thus the

gradients involved in the diffusional contribution become very small. It remains to be seen whether in experimentally feasible cases there is an accessible region near the critical point where Eqs. (4.1) and (4.8) are still valid and the diffusional contribution negligible.

In order to estimate the order of magnitude of the Q and S terms, it is convenient to transform Eq. (4.1) to a dimensionless form. To this end we assume that we can identify in our system a characteristic time θ (inverse of some characteristic rate), a characteristic diffusion coefficient δ and a characteristic concentration γ. The choice of these parameters is made such that the concentrations x, expressed in units of γ, the diffusion coefficients expressed in units of δ, and the reaction rates $M(\vec{r}+\vec{r}')$ expressed in units of γ/θ are all of order one [obviously scattering of a few orders of magnitude around $O(1)$ may be expected in particular cases]. Note that θ, δ, and γ define also a characteristic length $(\delta\theta)^{1/2}$ and a characteristic mass $\gamma(\delta\theta)^{d/2}$. We transform Eq. (4.1) into a dimensionless form by expressing all quantities in dimensionless (θ, δ, γ) units. Thus

$$\begin{aligned}
&\delta(\vec{r}-\vec{r}')\delta(t-t') \to (\delta\theta)^{d/2}\theta^{-1}\delta(\vec{r}-\vec{r}')\delta(t-t'),\\
&\nabla_r\nabla_{r'} \to (\delta\theta)^{-1}\nabla_r\nabla_{r'},\\
&\partial\vec{x}/\partial t \to (\gamma/\theta)(\partial\vec{x}/\partial t),\\
&\vec{\vec{D}}\cdot\nabla^2\vec{x} \to (\gamma/\theta)\vec{\vec{D}}\cdot\nabla^2\vec{x},\\
&\vec{F}(\vec{x}) \to (\gamma/\theta)\vec{F}(\vec{x}),
\end{aligned} \tag{4.9}$$

where all the quantities on the right-hand side besides θ, δ, and γ are dimensionless and of comparable orders. Equation (4.1) retains its form when written in terms of the dimensionless quantities and functions. The new, dimensionless parameters Q and S are given in terms of the old dimensioned quantities D, x, r_κ, etc. and in terms of θ, δ, and γ in the forms

$$Q \sim \frac{M}{A_0}\, M\left(\sum_\kappa \nu^2 r_\kappa\right)\frac{\theta(\delta\theta)^{-d/2}}{\gamma^2} \tag{4.10}$$

and

$$S \sim (Dx/A_0)[\theta(\delta\theta)^{-(d+2)/2}/\gamma^2]\,. \tag{4.11}$$

Taking

$$M\left(\sum_\kappa \nu^2 r_\kappa\right)(\theta/\gamma) \sim D/\delta \sim x/\gamma \sim 1\,, \tag{4.12}$$

we obtain

$$Q \sim (M/A_0)[(\delta\theta)^{-d/2}/\gamma]\,, \tag{4.13}$$

$$S \sim (1/A_0)[(\delta\theta)^{-d/2}/\gamma]. \tag{4.14}$$

We see that $Q \gtrsim S$ and thus close enough to the critical point ($\epsilon \ll 1$) we may indeed disregard the diffusional contributions to the random forces.

For a typical liquid system characterized by $\theta = 10^{-3}$ sec, $\delta = 10^{-5}$ cm^2/sec, $\gamma = 10^{-2}$ g/cm^3, and $M \sim 100$, we have, in three dimensions, $Q \sim 10^{-8}$. It is also of interest to consider the resolution in controlling the external parameter λ which determines the approach to the critical point. If λ measures a feeding rate for one of the chemicals in the system, a good resolution is probably $\sim 10^{-5}$ g/(sec cm^3) $= 10^{-5}\theta/\gamma$ in dimensionless units. For $\theta = 10^{-3}$ sec and $\gamma = 10^{-2}$ g/cm^3, we have[26] $\delta\lambda \sim \epsilon \geq 10^{-3}$. This is a bound on the closest measurable approach to the critical point in our system.[26]

Following Graham[3d] we now repeat the procedure described in Sec. III, this time starting from the stochastic equation (4.1). As long as $Q < \epsilon^{6-(d+2)}$ the stochastic force terms (with correlations given by Eq. (4.8) are of order ϵ^3 or higher and will not contribute before the third order. If we take the stochastic contribution to be $O(\epsilon^3)$, Eq. (3.27) will be modified by the appearance of a stochastic term (essentially $\vec{u}_0^{(1)}\cdot\vec{f}$) on the right-hand side. Equation (3.27) thus becomes a Langevin-Landau-Ginzburg equation for the order parameter W. It may be converted to a functional Fokker-Planck equation and a solution for the steady-state probability distribution may be obtained in terms of a general Landau-Ginzburg potential, as described in previous works.[22] This approach ceases to be valid too close to the critical point. The condition

$$Q < \epsilon^{4-d} \tag{4.15}$$

gives the corresponding limit of validity. We note that the dimensionality $d = 4$ naturally appears as a borderline: For $d < 4$ the theory breaks down for a close enough approach to the critical point. For $d > 4$ the theory is always valid. We further note that for $d = 3$, the condition $Q < \epsilon$ always holds for the choice of parameters as described above. It should be kept in mind, however, that other experimental situations may be imagined where the distance from the critical point is much better controlled than what was assumed before (e.g., variations of the light intensity in a photothermochemical instability).

It must be admitted that the procedure that we followed here[3d] is not entirely satisfactory. One would like to get a Langevin equation for the order parameter, if such equation is valid, without the need to consider the order of magnitude of Q relative to that of ϵ. We shall see that the condition (3.15) for the validity of the present approach holds as long as the Ginzburg criterion for the validity of mean-field theory is satisfied. This assures us that the derivation of this Ginzburg criterion in

Sec. VI is self-consistent. However, the present approach is not sufficient within the critical region itself. An approach based on Mori's scaling procedure[23] where, following van Kampen,[17] the deterministic and the stochastic motions are scaled differently, may be a better way to approach this problem. We leave this question open for future work.

V. ANALYSIS OF A MODEL

In this section we apply the theory presented in Secs. II-IV to an analysis of the Edelstein model.[24] This model is characterized by the set of chemical equations

$$\begin{aligned} &A'' + x \underset{\rightarrow}{\overset{1}{\underset{2}{\rightleftharpoons}}} 2x\,, \\ &x + y \underset{\rightarrow}{\overset{3}{\underset{4}{\rightleftharpoons}}} C + M\,, \\ &C + M \underset{\rightarrow}{\overset{5}{\underset{6}{\rightleftharpoons}}} y + B''\,. \end{aligned} \tag{5.1}$$

Here the concentrations A'', B'', M, and $K = C + y$ are externally controlled parameters, while x and y may be considered as the variables characterizing the state of the system. To have those features of the model retained also in a local description, including diffusion, we assume that y and C do not diffuse. The kinetic equation corresponding to (5.1) are

$$\begin{aligned} \partial x/\partial t &= D\nabla^2 x + k_1 A'' x - k_2 x^2 - k_3 xy + k_4 M(K - y), \\ \partial y/\partial t &= -k_3 xy + k_4 M(K - y) + k_5 M(K - y) + k_6 B'' y. \end{aligned} \tag{5.2}$$

We go over to dimensionless quantities by dividing by $k_4 MK$ and redefining the variables:

$$\begin{aligned} &k_4 M t \to t, \quad (D/k_4 M)\nabla^2 \to \nabla^2, \\ &y/K \to y, \quad x/K \to x. \end{aligned} \tag{5.3}$$

We then get

$$\begin{aligned} \partial x/\partial t &= \nabla^2 x + A' x - \beta x^2 - \alpha xy + 1 - y, \\ \partial y/\partial t &= -\alpha xy + 1 - y + k(1 - y) - B' y, \end{aligned} \tag{5.4}$$

where

$$\begin{aligned} &A' = k_1 A''/k_4 M, \quad B' = k_6 B''/k_4 M, \\ &\alpha = k_3 K/k_4 M, \quad \beta = k_2 K/k_4 M, \quad k = k_4/k_5\,. \end{aligned} \tag{5.5}$$

For definiteness we retain A' and B' as our control parameters and choose fixed values for the other parameters. We chose for the present specific example $\alpha = 9$, $\beta = 0.5$, $k = 3.5$. With this choice the steady-state equations may be written in the form

$$y = \tfrac{9}{2}\,/(9x + B' + \tfrac{9}{2}) \tag{5.6a}$$

$$\begin{aligned} F(x) = \tfrac{9}{2}x^3 + [\tfrac{1}{2}(B' + \tfrac{9}{2}) - 9A']\,x^2 \\ + [\tfrac{63}{2} - A'(B' + \tfrac{9}{2})]\,x - B' = 0. \end{aligned} \tag{5.6b}$$

Equation (5.6b) implies that there may be three homogeneous steady states coexisting. It can be shown that instabilities in this system occur first in the homogeneous mode. The critical point should satisfy Eqs. (5.6) together with $\partial F/\partial x = 0$ and $\partial^2 F/\partial x^2 = 0$. This provides four equations for determining A_c', B_c', x_c, and y_c. We obtain

$$A_c' = 2, \quad B_c' = \tfrac{9}{2}, \quad x_c = 1, \quad y_c = \tfrac{1}{4}. \tag{5.7}$$

In terms of the deviations from the critical point the equations of motion are

$$\partial\xi/\partial t = \nabla^2\xi - \tfrac{1}{2}\xi^2 - 9\xi\eta + (A - \tfrac{5}{4})\xi - 10\eta + A, \tag{5.8a}$$

$$\partial\eta/\partial t = -9\xi\eta - (B + 18)\eta - \tfrac{9}{4}\xi - \tfrac{1}{4}B\,, \tag{5.8b}$$

where

$$\begin{aligned} &A = A' - 2\,, \quad B = B' - \tfrac{9}{2}\,, \\ &\xi = x - 1, \quad \eta = y - \tfrac{1}{4}. \end{aligned} \tag{5.8c}$$

At the critical point $A = B = \xi = \eta = 0$, we have

$$\overleftrightarrow{\Omega}_c = \begin{pmatrix} -\frac{5}{4} & -10 \\ -\frac{9}{4} & -18 \end{pmatrix}, \tag{5.9a}$$

with its eigenvectors

$$u_0 = \frac{1}{\sqrt{77}}\begin{pmatrix} 8 \\ -1 \end{pmatrix}, \quad u_0^{(l)} = \frac{1}{\sqrt{77}}\begin{pmatrix} 9 \\ -5 \end{pmatrix} \tag{5.9b}$$

and

$$u_1 = \frac{1}{\sqrt{77}}\begin{pmatrix} 5 \\ 9 \end{pmatrix}, \quad u_1^{(l)} = \frac{1}{\sqrt{77}}\begin{pmatrix} 1 \\ 8 \end{pmatrix}. \tag{5.9c}$$

It is easily checked that the critical point conditions, Eqs. (2.7) and (2.18) [or (2.23), (2.25)] are satisfied for $A = B = 0$ at the critical point $\xi = \eta = 0$.

Turning now to the Langevin force terms, we use the theory of Sec. IV to rewrite Eqs. (5.8) in the form

$$\partial\xi/\partial t = \nabla^2\xi - \tfrac{1}{2}\xi^2 - 9\xi\eta + (A - \tfrac{5}{4})\xi - 10\eta + A + f_\xi(\vec{r}, t), \tag{5.10a}$$

$$\partial\eta/\partial t = -9\xi\eta - (B + 18)\eta - \tfrac{9}{4}\xi - \tfrac{1}{4}B + f_\eta(\vec{r}, t)\,, \tag{5.10b}$$

with

$$\begin{aligned} &\langle f_\xi(\vec{r}, t) f_\xi(\vec{r}', t')\rangle \\ &\quad = Q_\xi \delta(\vec{r} - \vec{r}')\delta(t - t') + S_\xi \nabla_r \cdot \nabla_{r'} \delta(\vec{r} - \vec{r}')\delta(t - t'), \end{aligned} \tag{5.11a}$$

$$\langle f_\eta(\vec{r}, t) f_\eta(\vec{r}', t')\rangle = Q_\eta \delta(\vec{r} - \vec{r}')\delta(t - t'), \tag{5.11b}$$

$$\langle f_\eta(\vec{r}, t) f_\xi(\vec{r}', t')\rangle = Q_{\xi\eta}\delta(\vec{r} - \vec{r}')\delta(t - t'). \tag{5.11c}$$

For the Q coefficients we obtain (using critical point values of all parameters and concentrations)

$$\begin{aligned} &Q_\xi = \tfrac{11}{2} I, \quad Q_\eta = \tfrac{27}{4} I, \\ &Q_{\xi\eta} = 3I, \quad S_\xi = (2/M_x) I, \end{aligned} \tag{5.12}$$

where

$$I=(1/A_0K)[D(k_4M)^{-1}]^{-d/2}, \tag{5.13}$$

d being the dimensionality of the system, and where M_x is the molecular weight of the diffusing species x. Note that in Eqs. (5.10)–(5.13) all concentrations are expressed in moles rather than in grams as was done in Sec. II. Taking this difference into account we readily see the connection to the general formulation of Sec. IV: D, which is the only diffusion coefficient in our problem, is identified with δ of Eqs. (4.13) and (4.14); the characteristic time is $\theta=(k_4M)^{-1}$ and the characteristic concentration is $\gamma=M_xK$.

Equations (5.10) lead to the following equation of state for ξ with A and B as controlled parameters

$$-\tfrac{9}{2}\xi^3+(9A-\tfrac{1}{2}B)\xi^2 +(B+27A+AB)\xi+(\tfrac{5}{2}B+18A+AB)=0. \tag{5.14}$$

η is uniquely determined in terms of ξ as

$$\eta=-(B+9\xi)/4(B+9\xi+18). \tag{5.15}$$

Consider now the approach to the critical point. This can be done in principle by keeping a certain linear combination of A and B zero, and studying the approach to zero along the orthogonal linear transformation. Based on the similarity of Eq. (5.14) to cubic equations of state appearing in the Landau theory of phase transitions, we can expect to encounter two types of parameters which may be called temperaturelike and magnetic-field-like. When a temperaturelike parameter T approaches the critical point ($T=0$, say) we expect a mean-field theory prediction $\xi,\eta\sim T^{1/2}$. When a magnetic-field-like parameter H does the same we expect $\xi,\eta\sim H^{1/3}$. Clearly, any linear combination of T and H must be magnetic-field-like. Only a unique combination of the physical parameters can be a temperaturelike variable.

From Eq. (5.14) it is easily realized that A and B are both magnetic-field-like parameters and that the only approach to criticality characterized by a temperaturelike behavior is the one for which $5B+36A=0$. We proceed to analyze the two different typical situations.

(i) A magnetic-field-type approach: Let $B=0$. As $A\to 0$ we have from Eqs. (5.14) and (5.15) the (A-dependent) steady-state values $\xi_0=(4A)^{1/3}$ and $\eta_0=-(\frac{1}{8})(4A)^{1/3}$. The matrix $\vec{\vec{\Omega}}_0(A)$ may be written in the form

$$\vec{\vec{\Omega}}_0=\vec{\vec{\Omega}}_c+(4A)^{1/3}\begin{pmatrix}\frac{1}{8} & -9\\ \frac{1}{8} & -9\end{pmatrix}+A\begin{pmatrix}1 & 0\\ 0 & 0\end{pmatrix}. \tag{5.16}$$

It is easily checked[25] that the root of $\vec{\vec{\Omega}}_0$ which vanishes when $A\to 0$ goes like $A^{2/3}$. We therefore relate $\delta\lambda$ not to A but to $A^{2/3}$, and put

$$\begin{aligned}&(4A)^{1/3}=\epsilon a,\\ &\partial/\partial t=\epsilon^2(\partial/\partial\tau),\\ &\partial/\partial r=\epsilon(\partial/\partial R),\\ &\vec{\vec{\Omega}}=\vec{\vec{\Omega}}_0+\epsilon a\vec{\vec{\Omega}}_1+O(\epsilon^3),\end{aligned} \tag{5.17}$$

where a ($=\sqrt{\delta\lambda}$) is a measure of the deviation from the critical point and where

$$\vec{\vec{\Omega}}_1=\begin{pmatrix}\frac{1}{8} & -9\\ \frac{9}{8} & -9\end{pmatrix} \tag{5.18}$$

is the matrix defined by Eq. (3.8). The following points concerning this expansion should be noted: (a) In contrast to the expected behavior of Sec. III there are no terms of order ϵ^2 in the expansion $\vec{\vec{\Omega}}$ around $\vec{\vec{\Omega}}_0$, (b) the term $O(\epsilon^3)$ in the expansion of $\vec{\vec{\Omega}}$ does not contribute to the ϵ expansion of the equations of motion up to the relevant third order and, (c) it can be checked using Eqs. (5.9b) and (5.18) that the matrix $\vec{\vec{\Omega}}_1$ has the property $\vec{u}_0^{(1)}\cdot\vec{\vec{\Omega}}_1\cdot\vec{u}_0=0$, in agreement with the results of Sec. III.

The asymptotic expansion of the equations of motion proceeds now along the lines described in Sec. III. The result is

$$(\partial/\partial\tau-\tfrac{72}{77}\nabla_R^2)W=-\tfrac{36}{77}(a^2W+12/\sqrt{77}\,aW^2+\tfrac{32}{77}W^3)+f_W, \tag{5.19}$$

where the new random source term is obtained from

$$f_W=\vec{u}_0^{(1)}\cdot\vec{f}$$

and where $W\vec{u}_0$ is the state vector measured from its (a-dependent) steady-state value. Transforming the origin to the critical point we obtain

$$\begin{pmatrix}\xi\\ \eta\end{pmatrix}=a\begin{pmatrix}1\\ -\frac{1}{8}\end{pmatrix}+W\vec{u}_0. \tag{5.20}$$

The analogy to a magnetic-field-type approach to criticality is seen by considering an equation of motion of the kind

$$\frac{dy}{dt}=z^3+H, \tag{5.21}$$

with a steady-state solution $z_0=-H^{1/3}$. Putting $z=z_0+z'$, the equation for z' becomes

$$\frac{dz'}{dt}=z'^3-3H^{1/3}z'^2+3H^{2/3}z, \tag{5.22}$$

which resembles Eq. (5.19) in which a plays the role of $H^{1/3}$.

(ii) A temperaturelike approach: Taking $B=-\frac{36}{5}A$ in Eq. (5.14) we obtain for $A\to 0_+$ the steady-state values $\xi_0=(\frac{22}{5}A)^{1/2}$ and $\eta_0=-\frac{1}{8}(\frac{22}{5}A)^{1/2}$. For $A\to 0_-$, $\xi_0=\eta_0=0$ is the only real solution. Consider first the case $A>0$. For this case

$$\vec{\Omega}_0=\vec{\Omega}_c+(\tfrac{22}{5}A)^{1/2}\vec{\Omega}_1+A\vec{\Omega}_2, \tag{5.23}$$

where $\vec{\Omega}_1$ is given by Eq. (5.18) and where

$$\vec{\Omega}_2=\begin{pmatrix}1 & 0\\ 0 & -\frac{36}{5}\end{pmatrix}. \tag{5.24}$$

The root of $\vec{\Omega}_0$ which vanishes as $A\to 0$ now goes like A. We define

$$A=\epsilon^2 b, \tag{5.25}$$

where b measures the distance from the critical point and plays the role of $\delta\lambda$ of Sec. III. Thus Eq. (5.23) becomes

$$\vec{\Omega}_0=\vec{\Omega}_c+\epsilon(\tfrac{22}{5}b)^{1/2}\vec{\Omega}_1+\epsilon^2 b\vec{\Omega}_2. \tag{5.26}$$

The expansion of the equations of motion goes now exactly as described in Sec. III, and leads to the following equation for the order parameter W:

$$(d/d\tau-0.94\nabla_R^2)W=2.26bW-1.01\sqrt{b}\,W^2-0.78W^3+f_W(\vec{R},\tau)\quad(b>0). \tag{5.27}$$

For the correlation function of f_W we get

$$\langle f_W(\vec{R},\tau)f_W(\vec{R}',\tau')\rangle=4.47I\delta(\vec{R}-\vec{R}')\delta(\tau-\tau') \tag{5.28}$$

where I is given by Eq. (5.13).

For $A<0$ we saw that ξ and η are zero at steady state. This implies that the $\vec{\Omega}_1$ term does not appear in the expansion of $\vec{\Omega}$ Eqs. (5.23) or (5.26). The expansion of the equations of motion now yields

$$(d/d\tau-0.94\nabla_R^2)W=0.47bW-0.78W^3+f_W(\vec{R},\tau)\quad(b<0), \tag{5.29}$$

where f_W is the same as in Eq. (5.27) and satisfies Eq. (5.28)

Equations (5.27) and (5.29) are exactly what we expect for time-dependent Ginzburg-Landau equations describing a temperaturelike deviation from the critical point. b stands here for the temperature variable. We point out that the form (5.29), which is similar to what is obtained in symmetry-breaking transitions,[5] is obtained in our example only in a very special case.

VI. GINZBURG CRITERION

A Langevin equation of the form

$$\frac{\partial}{\partial\tau}W=\sigma\nabla^2W+F(W)+f(\vec{r},t), \tag{6.1}$$

with f being a Gaussian random variable satisfying

$$\langle f(\vec{r},t)\rangle=0,$$
$$\langle f(\vec{r},t)f(\vec{r}'t')\rangle=\Phi\delta(\vec{r}-\vec{r}')\delta(t-t'), \tag{6.2}$$

is known to yield a steady-state probability distribution

$$P[W(r)]=\frac{1}{Z}\exp\left(-\frac{1}{\Phi}\int dr\{U[W(r)]+\tfrac{1}{2}\sigma[\nabla W(r)]^2\}\right), \tag{6.3}$$

where Z is a normalizing factor and U is related to F by

$$F(x)=-\partial U(x)/\partial x. \tag{6.4}$$

For the case

$$U(W)=\mu W^2+\tfrac{1}{2}\nu W^4. \tag{6.5}$$

Ginzburg[18] has provided a criterion for the validity of mean-field theory or of the Gaussian approximation (which neglects the quartic term). The Ginzburg criterion is, in our notation,

$$\frac{\Phi K_d\nu N}{(2\pi)^d(\frac{1}{2}\sigma)^2}\left(\frac{\frac{1}{2}\sigma}{\mu}\right)^{(4-d)/2}\ll 1, \tag{6.6}$$

where d is the dimensionality of the system; K_d, the surface area of a d-dimensional unit sphere; and where

$$N=\int_0^\infty dx\,\frac{x^{d'}}{1+x^2}, \tag{6.7}$$

with d' being the noninteger part of d. Equation (6.6) provides a measure for the size of the "critical region," near the critical point where mean-field theory or the Gaussian approximation fail. It can be directly applied to the time-dependent Ginzburg-Landau equation (5.29) that we obtained in studying the particular example of the Edelstein model. Of more interest is to see the relation between the Ginzburg criterion (6.6) and the condition $Q<\epsilon^{4-d}$ [Q is defined by Eq. (4.13)] for the validity of the asymptotic expansion of the stochastic equations of motion discussed in Sec. IV. Assuming

$$K_d\nu N\sigma^{-d/2}/(2\Pi)^d\sim O(1),$$

Eq. (6.6) yields

$$\Phi\ll\mu^{(4-d)/2}. \tag{6.8}$$

Comparing Eq. (6.5) to Eqs. (5.25) and (5.29) we see that μ should be identified with ϵ^2, and σ identified as the dimensionless diffusion coefficients.[26] Φ is equivalent to Q of Sec. III,

$$\Phi\equiv Q\sim(M/A_0)[(\delta\theta)^{-d/2}/\gamma]; \tag{6.9}$$

M, δ, θ, and γ being characteristic molecular weight, diffusion coefficient, time, and concentration, respectively. With these chosen correctly, the order of magnitude estimate which leads to Eq. (6.8) indeed holds. We conclude that the Ginzburg criterion can be identified as a condition for the validity of the expansion procedure

which leads to time-dependent Ginzburg-Landau equations of the kind obtained in this paper.

Equation (6.9) may be recast in the form

$$Q \sim 1/A_0 g\,, \tag{6.10}$$

where g is the characteristic amount of reactants (in moles) in the volume $(\delta\theta)^{-d/2}$. We have estimated in Sec. IV that in many cases the condition $Q < \epsilon$ (for $d = 3$) will always hold in any practical measurement. It should be pointed out however that chemical parameters, like concentrations and reaction rates, may have values ranging through many order of magnitude. For very fast reaction, and very low concentrations, very small values of g may be attained (e.g., $g \sim 10^{-29}$ mole for $\theta \sim 10^{-9}$ sec, $D \sim 10^{-5}$ cm^2/sec, and $\gamma \sim 10^{-8}$ mole/cm^3). Thus critical points of chemical instabilities potentially may give rise to breakdown of the mean-field picture and to nonclassical critical behavior. This is in contrast to other nonequilibrium phase transitions, i.e., the laser transition and the convection instability where for physically realizable parameters the true critical region is experimentally unattainable.

VII. CONCLUSION

In this paper we considered the critical behavior of a system where nonlinear chemical kinetics lead to the coexistence, far from equilibrium, of several homogeneous steady states. It was demonstrated that by imposing conditions which restrict the system to the vicinity of the critical point, the equations of motion can be reduced to yield a dynamic equation for the order parameter characterizing the system. As in treatments of symmetry-breaking transitions[5] the appropriate order parameter was identified as the amplitude W of the null vector $\tilde{u}_0$ of the critical matrix $\tilde{\tilde{\Omega}}_c$ in the first-order expression for the state vector $\tilde{x}$ near the critical point, $x - x_0(\lambda) = W\tilde{u}_0$.

We further discussed the effect of fluctuations on the critical behavior in a way which was shown to be valid outside the Ginzburg critical region. The size of this region was estimated and we concluded that although in many cases it is too small to be experimentally accessible, it is possible in principle to find chemical systems for which the critical region can be reached. In this case we expect a breakdown of the present theory and a "nonclassical" critical behavior in the sense used in equilibrium phenomena.

The treatment of fluctuations within the present approach is incomplete mainly because of the uncertainty involved in the scaling of the random force. Wunderlin and Haken[5b] argue that the random force scales as ϵ^3. If we accept their argument, the resulting TDGL equation is valid at any distance from the critical point. However these authors treat, specifically, a one-dimensional problem, and their argument fails for higher dimensionality. In the present paper it was shown that if we assume that the random force scales only according to its spatial and temporal dependence, the validity of the reduction procedure is determined essentially by the Ginzburg criterion. This argument can be extended to yield generalized Ginzburg criteria for other types of nonequilibrium critical phenomena.[27]

After this work was concluded we received a manuscript by Gardiner and Walls[28] in which an estimate of the critical region is provided for the particular case of the Schlogl model mentioned in Sec. I. Also the special nature of this example makes a direct comparison with our general result (Sec. VI) difficult, there is a qualitative agreement between the two results.

Presently there are not many systems for which a controlled approach to the critical point may be attempted. The best candidate seems to be the photothermochemical instability[8,9] where the fact that the system is taken away from equilibrium by physical means and not by chemical flows makes it more controllable than other chemically unstable systems. Another way to get more insight on the critical behavior of nonequilibrium chemically unstable systems is by computer simulations of the kind performed by Ortoleva and Yip.[29] We hope that such experimental and numerical studies will be used to test the present theory and to shed more light on the nonclassical behavior within the critical region.

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APPENDIX A: PARTIAL DIFFERENTIATION BY JACOBIAN CALCULUS

Here we prove the identity (2.12)

$$(\partial F_1/\partial x_1)_{F_2 \cdots F_n} = J/J_1\,, \tag{A1}$$

where

$$J = \partial(F_1 \cdots F_n)/\partial(x_1 \cdots x_n)\,, \tag{A2}$$

and where

$$J_1 = \partial(F_2 \cdots F_n)/\partial(x_2 \cdots x_n)\,. \tag{A3}$$

To prove Eq. (A1) we use the following identities from the calculus of Jacobians:

$$\frac{\partial(uv\cdots w)}{\partial(xy\cdots z)}=\left(\frac{\partial(xy\cdots z)}{\partial(uv\cdots w)}\right)^{-1}, \tag{A4}$$

$$\frac{\partial(uv\cdots w)}{\partial(xy\cdots z)}=\frac{\partial(uv\cdots w)}{\partial(rs\cdots t)}\,\frac{\partial(rs\cdots t)}{\partial(xy\cdots z)}, \tag{A5}$$

and

$$\left(\frac{\partial u}{\partial x}\right)_{y\cdots z}=\frac{\partial(uy\cdots z)}{\partial(xy\cdots z)}. \tag{A6}$$

Utilizing these identities we obtain

$$\begin{aligned}\left(\frac{\partial F_1}{\partial x_1}\right)_{F_2\cdots F_n}&=\frac{\partial(F_1F_2\cdots F_n)}{\partial(x_1x_2\cdots x_n)}\\&=\frac{\partial(F_1F_2\cdots F_n)}{\partial(x_1x_2\cdots x_n)}\,\frac{\partial(x_1x_2\cdots x_n)}{\partial(x_1F_2\cdots F_n)}\\&=J\left(\frac{\partial(x_2\cdots x_n)}{\partial(F_2\cdots F_n)}\right)_{x_1}=\frac{J}{J_1}.\end{aligned} \tag{A7}$$

Similarly we show [cf. (2.18)]

$$\left(\frac{\partial J}{\partial x_1}\right)_{F_2\cdots F_n}=\frac{\partial(JF_2\cdots F_n)}{\partial(x_1F_2\cdots F_n)}=\frac{\partial(JF_2\cdots F_n)}{\partial(x_1x_2\cdots x_n)}\Big/J_1, \tag{A8}$$

so that for $J_1\neq 0$ at the critical point, Eqs. (2.18) and (2.17) are equivalent.

APPENDIX B: STABILITY CONDITIONS FOR THE REDUCED SYSTEM

In Sec. II and Appendix A, we have seen that the marginal stability identities $J=0$ and $d\lambda(x)/dx=0$ are equivalent provided that $J_1=\partial(F_2\cdots F_n)/\partial(x_2\cdots x_n)\neq 0$. Here we discuss the significance of the condition $J_1\neq 0$. We require that this inequality will hold at the point of marginal stability. Thus holding x_1 fixed at its marginal stability value we require that the resulting new system remains stable as we change λ to approach the marginal stability point of the old system characterized by unrestricted x_1. To cast this in a more mathematical form consider the matrix $\vec{\vec{\Omega}}$ written in the form

$$\vec{\vec{\Omega}}=\begin{pmatrix}\dfrac{\partial F_1}{\partial x_1} & \vec{a}\\ \vec{b} & \vec{\vec{\Omega}}_1\end{pmatrix}, \tag{B1}$$

with $\vec{\vec{\Omega}}_1$, the matrix corresponding to the determinant J_1, and

$$\vec{a}=\left(\frac{\partial F_1}{\partial x_2},\frac{\partial F_1}{\partial x_3},\ldots,\frac{\partial F_1}{\partial x_n}\right), \tag{B2}$$

$$\vec{b}=\left(\frac{\partial F_2}{\partial x_1},\frac{\partial F_3}{\partial x_1},\ldots,\frac{\partial F_n}{\partial x_1}\right)^{\text{transpose}} \tag{B3}$$

Let $\vec{u}_0(\lambda)$ be the eigenvector of $\vec{\vec{\Omega}}_0(\lambda)$ corresponding to the eigenvalue which vanishes at marginal stability,

$$\vec{\vec{\Omega}}_0(\lambda)\cdot\vec{u}_0(\lambda)=0 \quad \text{for } \lambda=\lambda_{ms}, \tag{B4}$$

(λ_{ms} denotes the marginal stability value of λ). Let

$$\vec{u}_0(\lambda)=\begin{bmatrix}u_{01}\\ u_{02}\\ \cdot\\ \cdot\\ \cdot\\ u_{0n}\end{bmatrix}\equiv\begin{pmatrix}u_{01}\\ \vec{u}_0'\end{pmatrix}. \tag{B5}$$

Then

$$\vec{\vec{\Omega}}\cdot\vec{u}_0=u_{01}\frac{\partial\vec{F}}{\partial x_1}+\begin{pmatrix}\vec{a}\cdot\vec{u}_0'\\ \vec{\vec{\Omega}}_1\cdot\vec{u}_0'\end{pmatrix}, \tag{B6}$$

and for $\lambda\to\lambda_{ms}$ we get

$$\vec{\vec{\Omega}}_1\cdot\vec{u}_0'=u_{01}\begin{bmatrix}\partial F_2/\partial x_1\\ \cdot\\ \cdot\\ \cdot\\ \partial F_n/\partial x_1\end{bmatrix}, \quad \lambda=\lambda_{ms}. \tag{B7}$$

Thus $u_{01}(\lambda_{ms})\neq 0$ is a necessary condition for the nonsingular character of $\vec{\vec{\Omega}}_1(\lambda_{ms})$. This seems to be the only general condition and excluding pathological cases we expect that $u_{01}(\lambda_{ms})\neq 0$ insures the nonsingularity of $\vec{\vec{\Omega}}_1(\lambda_{ms})$.

APPENDIX C: EQUIVALENCE OF TWO CRITICAL POINT RELATIONS

Here we establish the equivalence between Eqs. (2.23) and (2.25). In Eq. (2.25) we insert the identities (see Appendix D)

$$\vec{u}_0=\begin{bmatrix}C_{11}\\ C_{12}\\ \cdot\\ \cdot\\ \cdot\\ C_{1n}\end{bmatrix}, \quad \vec{u}_0^{(i)}=\begin{bmatrix}C_{11}\\ C_{21}\\ \cdot\\ \cdot\\ \cdot\\ C_{ni}\end{bmatrix}, \tag{C1}$$

to obtain

$$\sum_{ijk=1}^{n}\frac{\partial^2G_i}{\partial x_j\partial x_k}C_{i1}C_{1j}C_{1k}=0. \tag{C2}$$

This has to be compared to Eq. (2.23) which may be written as

$$\sum_{ijk=1}^{n}\frac{\partial^2G_i}{\partial x_j\partial x_k}C_{ij}C_{1k}=0. \tag{C3}$$

We thus have to show that the coefficients of $\partial^2 G_i/\partial x_j \partial x_k$ are equal, up to multiplication by a constant, to each other. In Eq. (C2) the coefficient is $2C_{i1}C_{1j}C_{1k}$. In Eq. (C3) it is $C_{ij}C_{1k}+C_{ik}C_{1j}$. Indeed from Eq. (D2) we have $C_{ij}=C_{1j}C_{i1}/C_{11}$ and $C_{ik}=C_{1k}C_{i1}/C_{11}$. Thus

$$C_{ij}C_{1k}+C_{ik}C_{1j}=2C_{i1}C_{1j}C_{1k}/C_{11}, \tag{C4}$$

which establishes the equivalence between Eqs. (C2) and (C3).

APPENDIX D: PROOF OF EQ. (C1)

Here we show that for a singular matrix $\vec{\vec{\Omega}}$ having a single zero eigenvalue, the right eigenvector corresponding to this zero eigenvalue can be written

$$\vec{u}=\begin{bmatrix} C_{k1} \\ C_{k2} \\ \cdot \\ \cdot \\ \cdot \\ C_{kn} \end{bmatrix} \quad \text{for any } k, \tag{D1}$$

where C_{ij} is the cofactor of the term Ω_{ij} of $\vec{\vec{\Omega}}$. We note in passing that under the same conditions the identity

$$C_{ki}/C_{kj}=C_{li}/C_{lj}, \tag{D2}$$

implied by Eq. (D1), holds.

We start by rewriting the equation

$$\vec{\vec{\Omega}}\cdot\vec{u}=0 \tag{D3}$$

in the form

$$\vec{\vec{\Omega}}''\cdot\vec{u}=-\begin{bmatrix} \Omega_{1k} \\ \cdot \\ \cdot \\ \cdot \\ \Omega_{kk} \\ \cdot \\ \cdot \\ \cdot \\ \Omega_{nk} \end{bmatrix} u_k, \tag{D4}$$

where $\vec{\vec{\Omega}}''$ is an $n\times(n-1)$ matrix obtained from $\vec{\vec{\Omega}}$ by eliminating the kth column. Similarly $\vec{u}'$ is obtained from $\vec{u}$ by eliminating the kth row.

Next we eliminate the kth row of Eq. (D4), thus obtaining the $(n-1)\times(n-1)$ system

$$\vec{u}'=-\vec{\vec{\Omega}}'\cdot\vec{b}u_k, \tag{D5}$$

where $\vec{b}$ is the transpose of $(\Omega_{1k}\cdots\Omega_{k-1,k}, \Omega_{k+1,k}\cdots\Omega_{nk})$ and where $\vec{\vec{\Omega}}'$ is the $(n-1)\times(n-1)$ matrix obtained from $\vec{\vec{\Omega}}$ by eliminating its kth row and column. We may write

$$(\vec{\vec{\Omega}}')^{-1}=\vec{\vec{C}}'/\det(\vec{\vec{\Omega}}')=\vec{\vec{C}}/C_{kk}, \tag{D6}$$

where $\vec{\vec{C}}'$ is the cofactor matrix of $\vec{\vec{\Omega}}'$. As we are free to choose one term in the unnormalized vector $\vec{u}$, we take $u_k=C_{kk}$ so that

$$\vec{u}'=\vec{\vec{C}}'\vec{b}. \tag{D7}$$

A typical term from Eq. (D7) is

$$u_i'=\sum_{j=0}^{k-1} C'_{ji}\Omega_{jk}+\sum_{j=k+1}^{n} C'_{ji}\Omega_{jk}. \tag{D8}$$

By inspection it may be seen that this is just an expansion of the determinant C_{ki} in what was the kth column of the parent matrix $\vec{\vec{\Omega}}$. This concludes the proof of Eq. (D1).

APPENDIX E: COMMENTS ON SCALING

Here we bring arguments for the scaling assumed in Sec. III.

(i) *Time.* Our choice of λ makes $\delta\lambda$ proportional to the decay rate of the slow mode. This makes our slow time scale of order ϵ^2.

(ii) *Length.* The $k=0$ mode is the first to become unstable. The lifetime of associated modes of small finite k is proportional to $(Dk^2)^{-1}$, where D is the diffusion constants. Thus the vicinity of criticality in k space is defined by $k\sim\epsilon$.

(iii) *Amplitude.* Consider the equations of state

$$\vec{F}(\vec{x},\lambda)=0, \tag{E1}$$

and consider a variation of the parameter λ, and consequently of the variables $\vec{x}$, which leaves $\vec{F}$ invariant. Then[15]

$$\Delta\vec{F}=\frac{\partial\vec{F}}{\partial\vec{x}}\cdot\delta\vec{x}+\frac{1}{2}\frac{\partial^2\vec{F}}{\partial\vec{x}\partial\vec{x}}:\delta\vec{x}\delta\vec{x}+\frac{\partial\vec{F}}{\partial\lambda}\delta\lambda$$
$$+\frac{1}{2}\frac{\partial^2 F}{\partial\lambda^2}(\delta\lambda)^2+\frac{\partial^2 F}{\partial\vec{x}\partial\lambda}\delta\vec{x}\delta\lambda=0. \tag{E2}$$

We wish to show that the assumption $||\delta\vec{x}|| \sim O(\sqrt{\delta\lambda})$ is consistent with the critical conditions. Making this assumption we have up to order ϵ^2,

$$\left(\frac{\partial\vec{F}}{\partial\vec{x}}\right)_c\cdot\delta\vec{x}+\frac{1}{2}\left(\frac{\partial^2\vec{F}}{\partial\vec{x}\partial\vec{x}}\right)_c:\delta\vec{x}\delta\vec{x}+\left(\frac{\partial\vec{F}}{\partial\lambda}\right)_c\delta\lambda=0, \tag{E3}$$

where $(\ )_c$ denotes terms evaluated at the critical point. The right eigenvectors and the eigenvalues of the matrix $\vec{\vec{\Omega}}_c=(\partial\vec{F}/\partial\vec{x})_c$ are denoted $\vec{u}_j$ and γ_j, respectively, with $\gamma_0=0$. We also require the left eigenvectors defined by $\vec{\vec{\Omega}}_c\vec{u}_j^{(l)}=\gamma_j\vec{u}_j^{(l)}$. We now expand the vector $\delta\vec{x}$ in the set $\{\vec{u}_j\}$:

$$\delta\vec{x}=\sum_j \alpha_j\vec{u}_j=\alpha_0\vec{u}_0+\sum_{j\neq 0}\alpha_j\vec{u}_j. \tag{E4}$$

Inserting Eq. (E4) into (E3) we obtain

$$\sum_{j\neq 0}\alpha_j\gamma_j\vec{u}_j+\frac{1}{2}\left(\frac{\partial^2\vec{F}}{\partial\vec{x}\partial\vec{x}}\right)_c:\left[\alpha_0^2\vec{u}_0\vec{u}_0+\sum_{j\neq 0}\alpha_0\alpha_j\vec{u}_0\vec{u}_j+\sum_{j\neq 0}\sum_{k\neq 0}\alpha_j\alpha_k\vec{u}_j\vec{u}_k\right]+\left(\frac{\partial\vec{F}}{\partial\lambda}\right)_c\delta\lambda=0. \tag{E5}$$

Assuming that $\gamma_j\sim O(1)$ for $j\neq 0$ it is clear from Eq. (E5) that $\alpha_j\sim O(\delta\lambda)$ for $j\neq 0$. If we assume that α_0^2 is of the same order, we obtain

$$\sum_{j\neq 0}\alpha_j\gamma_j\vec{u}_j+\tfrac{1}{2}\alpha_0^2\left(\frac{\partial^2\vec{F}}{\partial\vec{x}\partial\vec{x}}\right)_c:\vec{u}_0\vec{u}_0+\left(\frac{\partial\vec{F}}{\partial\lambda}\right)_c\delta\lambda=0, \tag{E6}$$

where all the terms here were asserted to be $O(\epsilon^2)$. The consistency of our assumptions at the critical point is realized by noting that the first and last term in the left-hand side of Eq. (E6) are orthogonal to $\vec{u}_0$. This is certainly true for the first term, while for the last term it follows from

$$\left(\frac{d\vec{F}}{d\lambda}\right)_c=\vec{\Omega}_c\cdot\left(\frac{\partial\vec{x}}{\partial\lambda}\right)_c+\left(\frac{\partial\vec{F}}{\partial\lambda}\right)_c=0, \tag{E7}$$

so that taking a scalar product with $\vec{u}_0^{(1)}$ from the left we obtain

$$\vec{u}_0^{(1)}\cdot\left(\frac{\partial\vec{F}}{\partial\lambda}\right)_c=0. \tag{E8}$$

These two terms are orthogonal to $\vec{u}_0$ also near any other point of marginal stability. However, only at the critical point we have seen that the term $(\partial^2\vec{F}/\partial\vec{x}\partial\vec{x})_c\vec{u}_0\vec{u}_0$ is also orthogonal to $\vec{u}_0$ [cf. Eq. (2.25)]. This establishes the consistency of our assertion that α_0^2 is $O(\delta\lambda)$ near the critical point.

*A preliminary report of part of this work has been published in "Synergetics-A Workshop," edited by H. Haken (Springer, N.Y., 1977).

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[15]In the notation of this paper the vector $(\partial^2\vec{G}/\partial\vec{x}\partial\vec{x}):\vec{u}\vec{u}$ has the meaning $\sum_{ij}(\partial^2\vec{G}/\partial x_i\,\partial x_j)u_iu_j$.

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[26]Some confusion may be caused by interchanging the roles of ϵ and of $\sqrt{\delta\lambda}$ which seem at first sight to contradict Eq. (3.1). In the formal analysis of Sec. III ϵ

is the small parameter and $\delta\lambda$ is $O(1)$. However, in the final TDGL equation [e.g., Eq. (3.27)] it is sometimes convenient to transform back to the original laboratory scale. Then all the terms in the TDGL equation become $O(\epsilon^3)$ and $\delta\lambda$ is replaced by $\epsilon^2\delta\lambda \sim \epsilon^2$.

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