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Scaling and Ginzburg criteria for critical bifurcations in nonequilibrium reacting systems

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Critical conditions are obtained for bifurcation phenomena in nonequilibrium systems (chemical instabilities) which are appropriate for transitions between homogeneous steady states as well as for symmetry-breaking transitions to static structures. In the case of symmetry-breaking instabilities these criteria enable the theory to be applied to systems in any number of spatial dimensions, eliminating a restriction to one-dimensional systems encountered in other treatments. These critical conditions allow for the derivation of time-dependent Ginzburg-Landau (TDGL)-type equations for the critical-mode amplitude (the order parameter) that grows into the new macrostate beyond the critical point. For homogeneous transitions the usual TDGL equation is obtained. For the case of intrinsic symmetry breaking, TDGL equations are found for coupled order parameters corresponding to different directions in k space. In both the intrinsic and the extrinsic cases the TDGL equations are found to have nonlinear transport terms. When the TDGL equations are turned into Langevin equations, Ginzburg criteria (defining the region where mean-field theory breaks down) are derived. The critical dimensionality thus determined is 4 for homogeneous and intrinsic symmetry-breaking transitions, and 6 for the extrinsic symmetry-breaking case (under given mild technical conditions). Expressions for the size of the nonclassical critical regions are obtained for the different transitions in terms of characteristic parameters. For chemical instabilities these regions are in principle accessible.

I. INTRODUCTION

In the past few years several attempts have been made[1-6] to cast the dynamics of nonequilibrium of physical and chemical systems near their transition points in a form analogous to the time-dependent Ginzburg-Landau (TDGL) equation of equilibrium critical phenomena. The reduction of a given, sometimes complicated, set of kinetic equations [equations of motion (EOM)] to a simple, usually single, equation of the TDGL type is based on the separation of time and space scales between the mode (or modes) which become marginally stable at the transition point and the other modes. Near this point the dynamics are mainly determined by these critical modes, which are adiabatically followed by the other modes. Adiabatic-following methods, as well as multiple-time-and-space-scale perturbation expansions, have been used to achieve a reduction based on this feature.

In this paper we advance a scaling method for the reduction of the EOM's near a critical point. Our approach is based on the scaling method of Mori[7(a),(b)] and related multiple-scale-limit-cycle perturbation techniques. It is shown that the scaling idea can be utilized for extracting TDGL-type equations almost by inspection, and that it enables us to characterize different classes of transitions according to their characteristic scaling. Furthermore, starting from generalized Langevin equations and comparing the scaling of the random terms to that of the terms associated with the deterministic motion, we can extract information on the range of validity of mean-field theory for these different classes. These generalized Ginzburg criteria are associated with characteristic critical dimensionalities, $d=d_c$, above which mean-field theory always holds. For $d<d_c$ the stochastic motion dominates the dynamics inside the (generalized) Ginzburg regions, and our scaling picture breaks down.

We use this approach for three physically distinct cases. First, a TDGL equation and a Ginzburg measure are obtained for the neighborhood of the critical point of a multiple homogeneous steady-state system. This case is analogous to simple equilibrium critical phenomena. Second, the procedure is modified and applied to the case of an intrinsic symmetry-breaking transition where, at the bifurcation point, a structure of a finite characteristic length scale emerges. Finally, we also investigate the application of the scaling approach to the extrinsic symmetry-breaking instability where the longest-wavelength modes are the first to become unstable, and the structure obtained is strongly dependent on the size of the system. These different kinds of symmetry-breaking transitions are introduced and discussed in Ref. 8, and are reviewed in Sec. II.

This paper is organized as follows. In Sec. II we review the common types of critical points encountered in far-from-equilibrium physicochemical systems and describe their mathematical properties. In Sec. III we describe the scaling method as applied to these different transition types and demonstrate the usefulness of this method for the simple homogeneous case. TDGL equations for symmetry-breaking transitions are obtained in Secs. IV and V for the intrinsic and the extrinsic cases, respectively. In Sec. VI we discuss the scaling of Langevin equations and demonstrate that the critical dimensionality and the Ginzburg criterion may be obtained by inspection from the scaled equations. Finally, we discuss the problems associated with experimentally approaching the critical region and speculate on the possible extension of the scaling picture into this region.

II. BIFURCATION PHENOMENA AND CRITICAL POINTS

Our starting point is a set of nonlinear partial differential equations having the general form

$$\frac{\partial \underline{C}}{\partial t} = \underline{\mathcal{F}}(\underline{C}, \vec{\nabla}, t; \underline{\lambda}), \tag{2.1}$$

where $\underline{C}(\vec{r},t)$ is the set of variables characterizing the state of the system at any time, $\underline{\lambda}$ is a vector of externally controlled parameters, and $\underline{\underline{\mathcal{F}}}$ is a general functional of $\underline{C}$ and its spatial derivatives. In this paper the notation $\underline{\mathfrak{A}}$ is used for a vector in species space or in the external parameter space. $\underline{\underline{\mathfrak{A}}}$ denotes a matrix in species space. The notation $\vec{\mathfrak{A}}$ stands for a vector in coordinate space. The variables $\underline{C}$ will be called state variables, and in the autonomous case where $\underline{\underline{\mathcal{F}}}$ does not depend explicitly on t we shall refer to the steady-state equations $\underline{\mathcal{F}}(\underline{C}, \vec{\nabla}, \underline{\lambda}) = \underline{0}$ as the equations of state. We shall limit ourselves in this paper to this autonomous case. In studying chemical instabilities in reacting diffusing systems $\underline{\mathcal{F}}$ is usually assumed to have the form

$$\underline{\mathcal{F}}(\underline{C}, \vec{\nabla}, \underline{\lambda}) = \underline{\underline{D}}\nabla^2 \underline{C} + \underline{F}(\underline{C}, \underline{\lambda}), \tag{2.2}$$

where $\underline{F}$ is some nonlinear function of the concentrations and other state variables, all included in the vector $\underline{C}$. The operator obtained by linearizing $\underline{F}$ around a spatially uniform steady state $\underline{C}^0(\underline{\lambda})$ is denoted $\underline{\underline{\Gamma}}(\underline{\lambda}, \vec{\nabla})$ or more explicitly $\underline{\underline{\Gamma}}(\underline{C}^0(\underline{\lambda}), \underline{\lambda}, \vec{\nabla})$. For the case described by (2.2), we have

$$\underline{\underline{\Gamma}}(\underline{\lambda}, \vec{\nabla}) = \underline{\underline{\Omega}}(\underline{\lambda}) + \underline{\underline{D}}\nabla^2, \tag{2.3}$$

or, in $\vec{k}$ space,

$$\underline{\underline{\Gamma}}(\underline{\lambda}, k^2) = \underline{\underline{\Omega}}(\underline{\lambda}) - k^2 \underline{\underline{D}}, \tag{2.4}$$

where

$$\underline{\underline{\Omega}}(\underline{\lambda}) = \underline{\underline{\Omega}}(\underline{C}^0(\underline{\lambda}), \lambda) \equiv \left(\frac{\partial \underline{F}}{\partial \underline{C}}\right) \underline{C}^0(\underline{\lambda}), \underline{\lambda}. \tag{2.5}$$

We shall be interested mainly in transitions from a homogeneous branch of steady states (such as the thermodynamic branch, the extension from the equilibrium point by continuous variation of $\underline{\lambda}$ from its equilibrium value) to other branches characterized by different types of behavior. The principal types are as follows[9]: (i) A new stationary homogeneous state (multiple-steady-state system). (ii) An oscillation, usually of a limit-cycle type. (iii) A spatially structured stationary state. We shall distinguish[8] between two such types of structure: intrinsically determined and extrinsic, system-size dependent. (iv) Traveling structures—waves. (v) Chaotic spatiotemporal behavior. In principle, these transitions, in analogy to the equilibrium case, can be associated with a discontinuous jump in the state variables (hard or first-order transitions), or by a continuous change in these variables (soft or second-order transitions). Experimentally hard-transition points are only attainable transiently; these points will be always smeared due to fluctuations and be associated with hysterestis phenomena. We shall focus attention on soft-transition points (also called critical points) and the mathematical conditions characterizing these points (critical conditions) will also be shown to play a significant part in the scaling procedure.

We now discuss the mathematical properties of the critical points associated with some of these different transition types.

a. Transitions between homogeneous steady states. A typical example of this kind is shown in Figs. 1 and 2. Here the critical point is a cusp catastrophe on a steady-state surface representing one state variable, C, as a function of two external parameters, λ_1 and λ_2. With respect to one of the external parameters, λ_2 in Figs. 1 and 2, the critical point ($\underline{\lambda} = 0$) is characterized by

$$\left(\frac{\partial \lambda_2}{\partial C}\right)_{\underline{\lambda}=0} = \left(\frac{\partial^2 \lambda_2}{\partial C^2}\right)_{\underline{\lambda}=0} = 0. \tag{2.6}$$

For the case represented by (2.2), these condi-

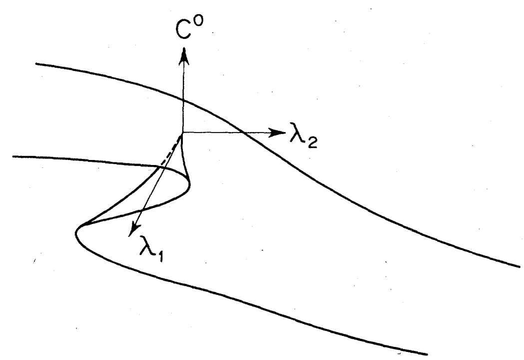

FIG. 1. Cusp catastrophe for nonequilibrium critical point unfolded in terms of external constraints λ_1 (temperaturelike variable) and λ_2 (magnetic-field-like variable). C^0 denotes a steady value of a descriptive variable such as concentration.

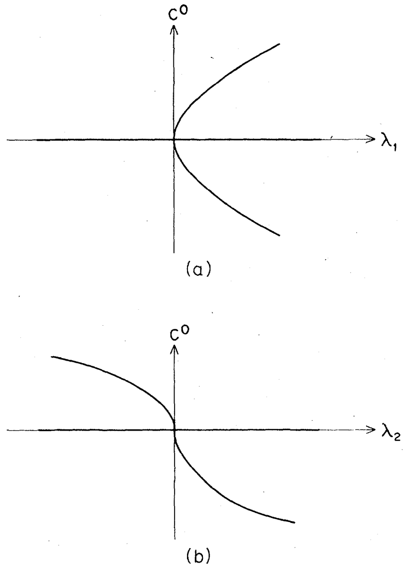

FIG. 2. Cross section of the cusp in the plane (a) $\lambda_2 = 0$ and (b) $\lambda_1 = 0$.

tions have been shown[3] to imply the equation

$$\left(\langle 0\underline{\lambda} \,|\, \sum_{ij} \frac{\partial^2 F}{\partial C_i \partial C_j} \,|\, 0\underline{\lambda}\rangle_i \,|\, 0\underline{\lambda}\rangle_j \right)_c = 0 \,, \tag{2.7}$$

where the vectors $|\,\alpha\lambda\rangle$ and $\langle\,\alpha\lambda\,|$ $(\alpha = 0, 1, 2, \ldots)$ are the sets (assumed complete) of right- and left-hand eigenvectors of the matrix $\underline{\underline{\Omega}}(\underline{\lambda})$,

$$\underline{\underline{\Omega}}(\underline{\lambda}) \,|\, \alpha\underline{\lambda}\rangle = \gamma_\alpha(\underline{\lambda}) \,|\, \alpha\underline{\lambda}\rangle \,, \tag{2.8}$$

and where $\alpha = 0$ corresponds to a root which vanishes at the critical point

$$\lim_{\underline{\lambda}\to 0} \gamma_0(\underline{\lambda}) = 0 \,. \tag{2.9}$$

The subscript c in (2.7) denotes the evaluation at the critical point. It is possible to shed more light on the number appearing on the left-hand side, of (2.7) by expressing the rate equations in terms of the amplitudes of the different eigenvectors. To this end we rewrite $\underline{F}$ of (2.2) in the form

$$\underline{F}(\underline{C}, \underline{\lambda}) = \underline{\underline{\Omega}}[\underline{C}^0(\underline{\lambda})\underline{\lambda}][\underline{C} - \underline{C}^0(\underline{\lambda})] + \underline{N}([\underline{C} - \underline{C}^0(\underline{\lambda})], \underline{C}^0(\underline{\lambda}), \underline{\lambda}) \,, \tag{2.10}$$

where $\underline{N}$ is a nonlinear function of quadratic or higher order in $\underline{C} - \underline{C}^0(\underline{\lambda})$. It is convenient to redefine the origin of the state variables such that

$$\underline{C} - \underline{C}^0(\underline{\lambda}) \to \underline{C} \,. \tag{2.11}$$

With this the equations of motion (EOM) (2.1) and (2.2) can be recast in the form

$$\frac{\partial \underline{C}}{\partial t} = \underline{\underline{D}}\vec{\nabla}^2 \underline{C} + \underline{\underline{\Omega}}[\underline{C}^0(\underline{\lambda}), \underline{\lambda}]\underline{C} + \underline{N}(\underline{C}, \underline{C}^0(\underline{\lambda}), \underline{\lambda}) \,, \tag{2.12}$$

$$(\underline{N})_l = \sum_{i,j} (\underline{\underline{N}}_2)^l_{ij} C_i C_j + \cdots \,, \tag{2.13}$$

where $\underline{\underline{N}}_2$ is the three-index tensor defined by

$$(\underline{\underline{N}}_2)^l_{ij} = \frac{1}{2}\left(\frac{\partial^2 F_l(\underline{C}, \underline{\lambda})}{\partial C_i \partial C_j}\right)_{\underline{C}^0(\underline{\lambda})} \,. \tag{2.14}$$

Next we expand the vector $\underline{C}$ of the state variables in the set $\{|\,\alpha\underline{\lambda}\rangle\}$

$$\underline{C} = \sum_\alpha M_\alpha(\vec{r}, t, \underline{\lambda}) \,|\, \alpha\underline{\lambda}\rangle \,. \tag{2.15}$$

Inserting into (2.12) and multiplying from the left by $\langle\,\beta\underline{\lambda}\,|$ we obtain

$$\frac{\partial M_\beta}{\partial t} = \sum_\alpha D_{\beta\alpha} \nabla^2 M_\alpha + \gamma_\beta M_\beta + \sum_{\alpha\alpha'} N^\beta{}_{\alpha\alpha'} M_\alpha M_{\alpha'} + \cdots \,, \tag{2.16}$$

where

$$D_{\beta\alpha} = \langle \beta\underline{\lambda} \,|\, \underline{\underline{D}} \,|\, \alpha\underline{\lambda}\rangle \,, \tag{2.17}$$

and

$$N^\beta_{\alpha\alpha'} = \langle\, \beta\underline{\lambda} \,|\, \underline{\underline{N}}_2 \colon |\, \alpha\underline{\lambda}\rangle \,|\, \alpha'\underline{\lambda}\rangle \,. \tag{2.18}$$

An expression $\langle a \,|\, \underline{\underline{N}}_2 \colon |\, b\rangle \,|\, c\rangle$ stands for the triple sum

$$\sum_{ijk} \frac{\partial^2 F_k}{\partial C_i \partial C_j} (\langle a\,|)_k (|\,b\rangle)_i (|\,c\rangle)_j \,,$$

where $(\langle a\,|)_i$ or $(|\,a\rangle)_i$ are components of the corresponding vectors. For $\alpha = \alpha' = \beta = 0$ the number appearing on the right-hand side of (2.18) is seen to be the coefficient of the term M_0^2 on the right-hand side of the equation for the mode amplitude M_0. This coefficient was shown[3] to vanish at the critical point defined by (2.6) for a system described by the EOM's (2.2). A central result of the present study is that the vanishing of this coefficient (or its equivalent in symmetry breaking and other instabilities) appears as a condition for a soft transition in more general cases.

b. Intrinsic symmetry breaking. By analogy to (2.8) we now introduce the eigenvalues and eigenvectors of the matrix $\underline{\underline{\Gamma}}(\lambda, k^2)$ given by (2.4),

$$\underline{\underline{\Gamma}}(\underline{\lambda}, k^2) \,|\, \alpha\underline{\lambda}k^2\rangle = \gamma_\alpha(\underline{\lambda}k^2) \,|\, \alpha\underline{\lambda}k^2\rangle \,, \tag{2.19}$$

with the corresponding left-hand eigenvectors $(\alpha\underline{\lambda}k^2\,|$. Consider now the case where all the parameters $\underline{\lambda}$ are held fixed except one (to be denoted λ) which is varied on the approach to the transition point. An intrinsic symmetry-breaking transition is characterized by the vanishing of at least one root, $\gamma_0(\lambda, k^2)$, at the transition point $\lambda = 0$, for $k = k_c \neq 0$. This situation is shown in Fig. 3, in which $\gamma_0(\lambda, k^2)$ is plotted against k^2 for different values of λ. Obviously this root satisfies

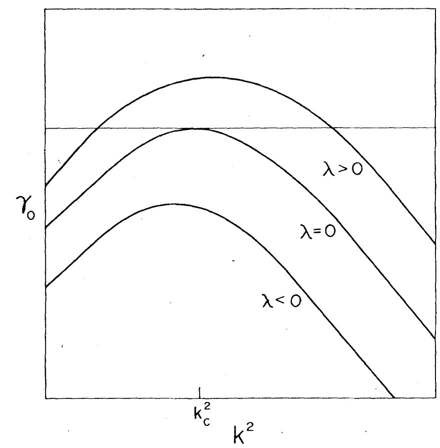

FIG. 3. Wave-vector (k) dependence of the eigenvalue (inverse relaxation time) $\gamma_0(\lambda, k^2)$ for various values of λ: < 0 (below), = 0 (at), and > 0 (above) the critical point for an intrinsic symmetry-breaking instability.

$$\left(\frac{\partial \gamma_0(0k^2)}{\partial(k^2)}\right)_{k^2=k_c^2} = 0 . \tag{2.20}$$

Defining

$$q = k_c^2 - k^2 , \tag{2.21}$$

$$\underline{\underline{\hat{\Gamma}}}(\lambda, k^2) = \underline{\underline{\hat{\Gamma}}}_0 + q\underline{\underline{D}} , \tag{2.22}$$

$$\underline{\underline{\hat{\Gamma}}}_0 = \underline{\underline{\hat{\Gamma}}}(\lambda, k_c^2) = \underline{\underline{\Omega}} - k_c^2 \underline{\underline{D}} , \tag{2.23}$$

we have for small q

$$\gamma_0(\lambda k^2) = \gamma_0(\lambda k_c^2) + \langle 0\lambda k_c^2 \mid \underline{\underline{D}} \mid 0\lambda k_c^2\rangle q + 0(q^2). \tag{2.24}$$

Equations (2.20) and (2.24) then lead to the result

$$\langle 00k_c^2 \mid \underline{\underline{D}} \mid 00k_c^2\rangle = 0 . \tag{2.25}$$

Moreover, since

$$[\underline{\underline{\Omega}}(0) - k_c^2 \underline{\underline{D}}] \mid 00k_c^2\rangle = 0 , \tag{2.26}$$

it follows that

$$\langle 00k_c^2 \mid \underline{\underline{\Omega}}(0) \mid 00k_c^2\rangle = 0 . \tag{2.27}$$

The relations (2.25) and (2.27) which characterize the intrinsic symmetry breaking transition were obtained using only properties of this transition displayed in Fig. 3 and do not rely on the existence of any critical conditions in the sense discussed for the homogeneous case via (2.6). However, as in that case, we expect that a reduced description of the system in the vicinity of the transition point is meaningful only in the case of soft transitions and we thus seek conditions under which this is indeed the case.

In discussing spatial symmetry-breaking transitions it is convenient to express the EOM's in terms of the amplitudes of the set of eigenvectors $\{\mid \alpha\lambda k^2\rangle\}$ of $\underline{\underline{\hat{\Gamma}}}$ (assuming this to be a complete set). A general solution to (2.12) is expanded in the form

$$\underline{C}(\vec{r}, t, \lambda) = \frac{1}{V}\sum_{\alpha,\vec{k}} M_{\vec{k}\alpha}(t) e^{i\vec{k}\cdot\vec{r}} \mid \alpha\lambda k^2\rangle . \tag{2.28}$$

This mode expansion is appropriate for a d-dimensional cubic system of volume V; $\vec{k}$ takes all values corresponding to periodic boundary conditions imposed on the system. Inserting (2.28) into (2.12), multiplying from the left-hand side by $\exp(-i\vec{k}\cdot\vec{r})\langle\alpha\lambda k^2 \mid$ and performing an integration over all space, we obtain

$$\frac{dM_{\vec{k}\alpha}}{dt} = \gamma_\alpha(\lambda k^2) M_{\vec{k}\alpha} + \sum_{\alpha_1\alpha_2}\sum_{\vec{k}'} \tilde{N}^{\alpha}_{\alpha_1\alpha_2}(\vec{k}\vec{k}'\lambda) \times M_{\vec{k}',\alpha_1} M_{\vec{k}-\vec{k}',\alpha_2} + \cdots . \tag{2.29}$$

We have used

$$\frac{1}{V}\int d\vec{r} \exp[i(\vec{k}-\vec{k}')\cdot\vec{r}] = \delta_{\vec{k}\vec{k}'}, \tag{2.30}$$

and set

$$\tilde{N}^{\alpha}_{\alpha_1\alpha_2}(\vec{k}\vec{k}'\lambda) \equiv \frac{1}{V}\langle \alpha\lambda k^2 \mid \underline{\underline{N}}_2 : \mid \alpha_1\lambda k'^2\rangle \mid \alpha_2\lambda(\vec{k}-\vec{k}')^2\rangle . \tag{2.31}$$

Note that (2.31) is equivalent to (2.18) when the eigenvectors of $\underline{\underline{\Gamma}}(\lambda, k^2)$ are replaced by those of $\underline{\underline{\Omega}}(\lambda)$. Clearly

$$\mid \alpha\lambda\rangle = \mid \alpha\lambda 0\rangle . \tag{2.32}$$

Also the parameters $\tilde{N}^{\alpha}_{\alpha_1\alpha_2}$ depend on the relative orientation of the vectors $\vec{k}, \vec{k}'$ as well as on their magnitudes.

It is shown in Appendix A using bifurcation theory (and later using scaling theory) that in order to have a soft transition for $d > 1$ a condition similar to (2.7) has to be satisfied, namely,

$$\langle\langle 00k_c^2 \mid \underline{\underline{N}}_2 : \mid 00k_c^2\rangle \mid 00k_c^2\rangle\rangle_c = 0 . \tag{2.33}$$

The bifurcation analysis of the present model near an intrinsic symmetry-breaking transition has been done earlier for one-dimensional structures by Wunderlin and Haken[2(a)] and by Kuramoto.[1] These authors encountered difficulties for structures of greater dimensionalties. In Appendix A, using bifurcation theory, we show that these difficulties can be resolved and a reduction of the equations of motion can be carried out for all d, provided we apply different scaling in the expansion procedure depending on whether (2.33) is satisfied or not.

For the direct scaling approach addressed in the present paper it turns out to be convenient to apply a represenatation which is intermediate between the coordinate representation (2.12) and the "normal-mode" picture (2.29). Rewrite Eq. (2.12) in the form

$$\frac{\partial \underline{C}}{\partial t} = \underline{\underline{D}}(\nabla^2 + k_c^2)\underline{C} + [\underline{\underline{\Omega}}(\lambda) - k_c^2 \underline{\underline{D}}]\underline{C} + \underline{\underline{N}}:\ \underline{C}\underline{C} + \cdots , \tag{2.34}$$

and expand

$$\underline{C}(\vec{r},t;\lambda) = \sum_\alpha M_\alpha(\vec{r},t;\lambda) \mid \alpha\lambda k_c^2\rangle , \tag{2.35}$$

where $|\alpha\lambda k_c^2\rangle$ are eigenvectors of $\underline{\underline{\Gamma}}_0$[see (2.23)]

$$\underline{\underline{\Gamma}}_0 | \alpha\lambda k_c^2\rangle = \gamma_\alpha(\lambda k_c^2) \mid \alpha\lambda k_c^2\rangle .$$

Inserting (2.35) into (2.34) and multiplying by $\langle\beta\lambda k_c^2|$, we obtain an equation for the amplitudes M_β:

$$\frac{\partial M_\beta}{\partial t} = \sum_\alpha \beta\lambda k_c^2 | \underline{\underline{D}} | \alpha\lambda k_c^2\rangle(\nabla^2 + k_c^2)M_\alpha + \gamma_\beta(\lambda k_c^2)M_\beta + \sum_{\alpha\alpha'} N^\beta_{\alpha\alpha'}(\lambda)M_\alpha M_{\alpha'} + \cdots . \tag{2.36}$$

We have assumed that the right- and left-hand eigenvectors of $\underline{\Gamma}_0$ constitute a complete biorthogonal set and introduced the notation

$$N^\beta_{\alpha\alpha'}(\lambda) = \langle\beta\lambda k_c^2 | \underline{\underline{N}}_2 : |\alpha\lambda k_c^2\rangle \mid \alpha'\lambda k_c^2\rangle . \tag{2.37}$$

$N^\beta_{\alpha\alpha'}$ is seen to be somewhat different from $\tilde{N}^\beta_{\alpha\alpha'}$ defined by (2.31). In terms of $N^\beta_{\alpha\alpha'}$ a necessary condition for soft transition (3.22) takes the form

$$N^0_{00}(0) = 0 . \tag{2.38}$$

Equation (2.36) is the starting point for the scaling treatment advances in Sec. IV. We note in passing that Eq. (2.18) is a special case of (2.37) for $k_c = 0$.

c. Extrinsic symmetry breaking. The instability in this case occurs first (at $\lambda = 0$) for $k = 0$, but for $\lambda > 0$ modes with $k \neq 0$ take over. A typical situation of this kind is shown in Fig. 4, where $\gamma_0(\lambda k^2)$ is plotted against k^2 for different values of λ. At the transition point we again have

$$\langle 000 | \underline{\underline{D}} | 000\rangle = 0 \tag{2.39}$$

which holds for the same reasons that lead to (2.25). Also the (in this case necessary) condition for critical (soft) behavior is identical to the $k_c = 0$ analog of (2.33) [which is identical to the homogeneous condition (2.7).]

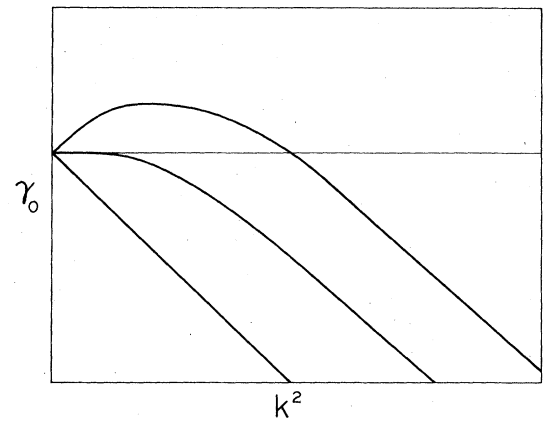

FIG. 4. Same as Fig. 3 for extrinsic symmetry breaking.

III. SCALING

As in equilibrium critical phenomena the scaling idea is based on the observation that close to a nonequilibrium critical point the critical mode(s) are characterized by slow and long-range variations. The idea is to scale space, time, and the mode amplitudes with the approach to the critical point such that the relevant terms in the dynamic equations remain invariant in form under this scaling. In fact the relevant terms are identified as those which remain invariant under this scaling and this requirement also leads to useful relations between the critical exponents.

In order to describe the essential features of the scaling procedure we focus first on a critical point for which a single homogeneous mode of the linearized system becomes soft (corresponding eigenvalus vanishes). In order to focus on the time and length scales associated with this soft mode as $\lambda \to 0$, we scale the variables in the following way: length,

$$\vec{r} = L\vec{r}\,' ; \tag{3.1a}$$

wave vector,

$$\vec{k} = L^{-1}\vec{k}\,' ; \tag{3.1b}$$

time,

$$t = L^z t' ; \tag{3.1c}$$

bifurcation parameters,

$$\lambda_i = L^{-y_i}\lambda_i' ; \tag{3.1d}$$

modes,

$$M_\alpha(\vec{r},t,\lambda) \sim M'_\alpha(\vec{r},t,\lambda)$$

and

$$M'_\alpha(\vec{r},t,\lambda) = L^{-x_\alpha}M'_\alpha(\vec{r}\,',t',\lambda') \tag{3.1e}$$

or

$$M_{\vec{q}\alpha}(t,\lambda) \sim M'_{\vec{q}\alpha}(t,\lambda)$$

and

$$M'_{\vec{q}\alpha}(t,\lambda) = L^{d-x_\alpha} M'_{\vec{q}'\alpha}(t',\lambda') . \quad (3.1f)$$

The physical picture behind this scaling is as follows. As the critical point is approached, the time and length scales associated with the critical modes diverge. We make the scaling hypothesis that sufficiently close to the critical point, the only relevant length and time that characterizes the solution of interest are proportional to some power of a scaling factor L. The factor L is chosen to be the characteristic length for convenience. If the scaling hypothesis is correct then the appropriate spatial variable is clearly $\vec{r}' = \vec{r}/L$, i.e., $\vec{r}$ scaled by the characteristic length L. Similar comments justify the introduction of the new variables t' and λ_i'. Since we do not know *a priori* to what power of L the characteristic time diverges we must, as we shall see, determine it from the equations of motion (and similarly for the exponents associated with the λ_i). According to the scaling hypothesis the only relevant length and time scales near the critical point are L and L^z for a system close to the critical point at a distance of order L^{-y_i} in the parameter λ_i. Thus since all the characteristic magnitudes have been absorbed into the primed variables the only effect a change of L can have on the mode coordinate is to multiply it by some function, assumed to be a power, of L. This justifies the scaling properties in the quantities M' given in (2.1e) and (2.1f).[10] Furthermore, we may require that all the relevant terms in the equations of motion become of order unity under this scaling. This enables us to find relations between the scaling exponents and to calculate them.

This procedure naturally brings out the fact that on the time and length scale relevant to the critical mode, the noncritical motion effectively comes to a steady state consistent with the instantaneous state of the critical mode(s) (see below). It thus contains the essential elements of the adiabatic-following procedures used in similar contexts.[2]

To demonstrate the way this method works, we consider a system of several reacting diffusing species characterized by the EOM's,

$$\frac{\partial \underline{C}}{\partial t} = \underline{\underline{D}}\,\nabla^2 \underline{C} + \underline{F}(\underline{C},\underline{\lambda}) . \quad (3.2)$$

By following the transformation described in Sec. II, (3.2) leads to (2.16). We take $\gamma_0(\underline{\lambda})$ to satisfy near $\lambda_i = 0$

$$\gamma_0(\lambda_i, \{\lambda_{j\neq i} = 0\}) \sim \lambda_i^{u_i} . \quad (3.3)$$

Let us rewrite (2.16) showing explicitly the terms corresponding to the critical mode:

$$\frac{\partial M_0}{\partial t} = D_{00}\nabla^2 M_0 + \gamma_0 M_0 + \sum_{\alpha\neq 0} D_{0\alpha}\nabla^2 M_\alpha + N^0_{00} M_0^2 + 2\sum_{\alpha\neq 0} N^0_{0\alpha} M_0 M_\alpha + \sum_{\alpha\alpha'\neq 0} N^0_{\alpha\alpha'} M_\alpha M_{\alpha'} . \quad (3.4)$$

$$\frac{\partial M_\alpha}{\partial t} = D_{\alpha 0}\nabla^2 M_0 + \sum_{\beta\neq 0} D_{\alpha\beta}\nabla^2 M_\beta + \gamma_\alpha M_\alpha + 2\sum_{\beta\neq 0} N^\alpha_{0\beta} M_0 M_\beta + \sum_{\beta\beta'\neq 0} N^\alpha_{\beta\beta'} M_\beta M_{\beta'} + N^\alpha_{00} M_0^2, \quad \alpha \neq 0 . \quad (3.5)$$

We note that (3.1d) and (3.3) imply the scaling property of the eigenvalues γ_α. Assume that all the parameters $\underline{\lambda}$ are zero except one that we denote λ. Then if, near $\lambda = 0$, $\gamma_0 = \lambda^u \gamma_0'$, we have

$$\gamma_0 = L^{-v}\gamma_0' , \quad v = yu . \quad (3.6)$$

On the other hand, γ_α for $\alpha \neq 0$ is (by the assumption of the existence of only one critical mode) of order zero in λ_i and is scale invariant

$$\gamma_\alpha = \gamma'_\alpha , \quad \alpha \neq 0 . \quad (3.7)$$

In addition, we recall that at the critical point $N^0_{00}(0) = 0$ [cf. (2.7)]. As $\lambda_i \to 0$, $N^0_{00}(\lambda)$ usually vanishes either as λ or as $\underline{C}^0(\lambda) - \underline{C}^0(0)$ (for bilinear nonlinearity $N^0_{00} \sim \lambda$ is the usual case, while for higher-order nonlinearities the second case becomes possible). To cover these various cases we take

$$N^0_{00} = L^{-w} N'^0_{00} , \quad w > 0 \quad (3.8)$$

where w can be calculated from (3.1d) and the known dependence of $N^0_{00}(\lambda)$ on λ for a given model. Other components of N are taken to be scale invariant

$$N^\alpha_{\beta\gamma} = N'^\alpha_{\beta\gamma} \quad (\alpha, \beta, \gamma \text{ not all } 0) . \quad (3.9)$$

Performing now the scaling described by (2.1) and (3.6)–(3.9) on (3.4) and (3.5), we obtain

$$\frac{\partial M_0'}{\partial t'} = L^{z-2} D_{00}\nabla'^2 M_0' + L^{z-v}\gamma_0' M_0' + L^{z-w-x_0} N'^0_{00} M_0'^2 + 2\sum_{\alpha\neq 0} L^{z-x_0} N^0_{0\alpha} M_0' M_\alpha' + L^{z+x_0-2}\sum_{\alpha\neq 0} L^{-x_\beta} D_{\alpha\beta}\nabla'^2 M_\alpha' + L^{z+x_0}\sum_{\alpha\alpha'\neq 0} L^{-x_\alpha - x_{\alpha'}} N^0_{\alpha\alpha'} M_\alpha' M_{\alpha'}' . \quad (3.10)$$

$$L^{-z}\frac{\partial M_\alpha'}{\partial t'} = L^{x_\alpha - x_0 - 2} D_{\alpha 0}\nabla'^2 M_0' + L^{x_\alpha - 2}\sum_{\beta\neq 0} L^{-x_\beta} D_{\alpha\beta}\nabla'^2 M_\beta' + \gamma'_\alpha M_\alpha' + L^{x_\alpha - 2x_0} N^\alpha_{00} M_0'^2 + 2L^{x_\alpha - x_0}\sum_{\beta\neq 0} L^{-x_\beta} N^\alpha_{0\beta} M_0' M_\beta' + L^{x_\alpha}\sum_{\beta\beta'\neq 0} L^{-x_\beta - x_{\beta'}} N^\alpha_{\beta\beta'} M_\beta' M_{\beta'}' . \quad (3.11)$$

Equation (3.10) suggests that the following relations should be satisfied by the scaling exponents in order that the full slow spatial and temporal evolution be maintained:

$$2=z=v=x_\alpha(\alpha\neq 0)\leq w+x_0\,. \tag{3.12}$$

The two last terms of (3.10) are irrelevant; i.e., they do not contribute to the long-scale solution since they have a persistent inverse factor of L after the scaling. The $M_0'^2$ term is relevant only provided $z=w+x_0$, and is irrelevant if the inequality in (3.12) holds. In (3.11) all terms but the $\gamma'_\alpha M'_\alpha$ and the $M_\alpha'^2$ terms are irrelevant i.e., as $L\to\infty$ (3.11) reduces to

$$\gamma'_\alpha M'_\alpha=-N_{00}'^{\alpha}M_0'^2\,, \tag{3.13}$$

provided

$$x_\alpha=2x_0\,. \tag{3.14}$$

Equation (3.13) states that on the long scale the fast modes come to steady state consistent with the value of the slow mode, the so-called adiabatic following. Combining these results we obtain a single equation of motion for the critical mode:

$$\frac{\partial M_0}{\partial t}=D_{00}\nabla^2M_0+\gamma_0M_0-2\left(\sum_{\alpha\neq 0}\frac{N_{0\alpha}^0N_{00}^\alpha}{\gamma_0}\right)M_0^3\quad(+N_{00}^0M_0^2)\,, \tag{3.15}$$

where the primes denoting scaled variables have been omitted. The last bracketed term appears only if $w=x_0=1$ and does not appear if $w>1$. This scaling result does not hold for $w<1$.

It is interesting to note that result (3.15) was obtained without specifying the direction of approach to the critical point [i.e., the choice of λ in (3.3), etc.]. To understand the significance of this result, consider the case represented by Fig. 1, where the critical point is a cusp on the steady-state surface plotted in a space of one state variable and two external parameters λ_1 and λ_2. The approach to the critical point along the λ_1 and the λ_2 directions is shown in Fig. 2. We see that in the first case $M_0\sim\lambda_1^{1/2}$ while in the second case $M_0\sim\lambda_2^{1/3}$. Recalling the analogy to magnetic critical phenomena, it is appropriate to call λ_1 a temperaturelike variable, and λ_2, a magnetic-field-like variable. We note in passing that any other direction of approach, defined as a linear combination $\lambda=A\lambda_1+B\lambda_2$, corresponds to the magnetic field type since $M_0\sim\lambda^{1/3}$ as $\lambda\to 0$. Now, (3.12) and (3.14) imply $x_0=1$, so that from (3.1d) we obtain

$$y_1=2\,,\quad y_2=3\,. \tag{3.16}$$

If, as is often the case, N_{00}^0 is proportional to λ_i [i.e., $w=y_i$ in (3.8)] the M_0^2 term in (3.15) will be absent. Note that the absence of a constant term in the equation is due to the fact that M_0 measures the deviation of the state variables from the ($\underline{\lambda}$-dependent) steady state and not from their values at the critical point. In this respect the development here differs from that of Ref. 3.

IV. SCALING FOR SYMMETRY-BREAKING TRANSITIONS WITH INTRINSIC LENGTHS

We are interested in the case where there is a critical mode of a wave vector of length k_c with a lifetime that diverges as a parameter λ attains a critical value zero as seen in Fig. 3. Clearly in these systems fluctuations with a wave vector on or near the critical shell, $|k|=k_c$ are of greatest amplitude. We shall refer to these as fluctuations on the critical scale (CS).

To apply the scaling procedure in the vicinity of a symmetry-breaking transition it is convenient to start from (2.36). We write it separately for the critical mode and for the other modes.

$$\begin{aligned}\frac{\partial M_0}{\partial t}=&\langle 0\lambda k_c^2|\underline{\underline{D}}|0\lambda k_c^2\rangle(\nabla^2+k_c^2)M_0+\sum_{\alpha\neq 0}\langle 0\lambda k_c^2|\underline{\underline{D}}|\alpha\lambda k_c^2\rangle(\nabla^2+k_c^2)M_\alpha\\&+\gamma_0(\lambda k_c^2)M_0+N_{00}^0(\lambda)M_0^2+2\sum_{\alpha\neq 0}N_{0\alpha}^0(\lambda)M_0M_\alpha+\sum_{\alpha\alpha'\neq 0}N_{\alpha\alpha'}^0(\lambda)M_\alpha M_{\alpha'}\,.\end{aligned} \tag{4.1a}$$

$$\begin{aligned}\frac{\partial M_\alpha}{\partial t}=&\langle\alpha\lambda k_c^2|\underline{\underline{D}}|0\lambda k_c^2\rangle(\nabla^2+k_c^2)M_0+\sum_{\alpha'\neq 0}\langle\alpha\lambda k_c^2|\underline{\underline{D}}|\alpha'\lambda k_c^2\rangle(\nabla^2+k_c^2)M_{\alpha'}\\&+\gamma_\alpha(\lambda k_c^2)M_\alpha+N_{00}^\alpha(\lambda)M_0^2+2\sum_{\alpha'\neq 0}N_{0\alpha'}^\alpha(\lambda)M_0M_{\alpha'}+\sum_{\alpha'\alpha''\neq 0}N_{\alpha'\alpha''}^\alpha(\lambda)M_{\alpha'}M_{\alpha''}\,,\quad\alpha\neq 0\,.\end{aligned} \tag{4.1b}$$

For simplicity we consider specifically the quadratic nonlinearity. Higher-order nonlinearities present no special difficulties. Also we focus attention on the soft-transition case characterized by (2.38). We assume that the terms $\langle 0\lambda k_c^2|\underline{\underline{D}}|0\lambda k_c^2\rangle$, $\gamma_0(\lambda,k_c^2)$ and $N_{00}^0(\lambda)$ are all of order λ.

Since we are interested in the long-time CS evolution of the system, we expect the relevant solution to be a linear combination of terms of the form $W(\vec{r},t)e^{(i\vec{k}_c\cdot\vec{r})}$ with $W(\vec{r},t)$ weakly dependent on $\vec{r}$ and t, and with different terms corresponding to $\vec{k}_c$ vectors having different directions. It should be kept in mind that such terms are always coupled to higher harmonics. The most general expansion of the function $M_\alpha(\vec{r}, t, \lambda)$ may be represented in the form

$$M_\alpha(\vec{r}, t, \lambda) = \sum_{n=1}^{\infty} \sum_{\{I\}_n} W_{\alpha\{I\}_n}^{(n)}(\vec{r}, t, \lambda) \exp\left(i \sum_{l=1}^{n} \vec{k}_c^{I_l} \cdot \vec{r}\right), \tag{4.2a}$$

where $\{I\}_n$ represents a group of n directions $(I_1, I_2 \ldots I_n)$ characterizing the vectors $\vec{k}_c^I(|\vec{k}_c^I| = k_c)$. Near the bifurcation point we expect the CS contribution to be dominant, i.e.,

$$\lim_{\lambda \to 0} M_\alpha(\vec{r} t \lambda) = \sum_I W_{\alpha I}(\vec{r}, t, \lambda) \exp(i\vec{k}_c^I \cdot \vec{r}) . \tag{4.2b}$$

Indeed, combination terms in Eq. (4.2a) are related to products of fundamental terms (obtained because of the nonlinearity of the problem). They therefore scale like higher powers of the distance from the critical point and disappear more rapidly than the fundamentals.

For the following discussion it is convenient to separate the sum (4.2a) in the form

$$M_\alpha = M_\alpha^{CS} + M_\alpha^{NS} , \tag{4.3}$$

where M_α^{CS} includes all those terms for which

$$\left| \sum_{l=1}^{n} \vec{k}_c^{I_l} \right| = k_c$$

(critical-scale terms) while M_α^{NS} includes all other terms.

The scaling defined by Eq. (3.1) has to be modified for the present case in two ways

(a) The scaling implied by Eq. (3.1) holds now only for the slowly varying (in space) parts W of the functions M. Consider a general term

$$f(\vec{r}, t, \lambda) = W(\vec{r}, t, \lambda) \exp(i\vec{k} \cdot \vec{r})$$

(belonging to M^{CS} for $|\vec{k}| = k_c$ and to M^{NS} otherwise). As only the $\vec{r}$ and t dependence of $W(\vec{r}, t)$ have scaling behavior, it is convenient to introduce two length variables

$$f(\vec{r}_1, \vec{r}_0, t, \lambda) = W(\vec{r}_1, t, \lambda) \exp(i\vec{k} \cdot \vec{r}_0) . \tag{4.4}$$

Equation (3.1) is now replaced by

$$\vec{r}_0 = \vec{r}_0' , \tag{4.5a}$$

$$\vec{r}_1 = L\vec{r}_1' , \tag{4.5b}$$

$$t = L^2 t' , \tag{4.5c}$$

$$\lambda = L^{-y} \lambda' , \tag{4.5d}$$

and

$$W(\vec{r}_1, t, \lambda) \sim W'(\vec{r}_1, t, \lambda) = L^{-x} W'(\vec{r}_1', t', \lambda') . \tag{4.5e}$$

Accordingly we write

$$\Delta = \Delta_0 + \Delta_1 + \Delta_2 , \tag{4.6}$$

where

$$\Delta_0 = \nabla_0^2 + k_c^2 , \quad \Delta_1 = 2\vec{\nabla}_0 \cdot \vec{\nabla}_1 , \quad \Delta_2 = \nabla_1^2 . \tag{4.7}$$

Under scaling $\vec{\nabla}_1 = L^{-1}\vec{\nabla}_1'$ so that $\Delta_0 = \Delta_0'$, $\Delta_1 = L^{-1}\Delta_1'$, $\Delta_2 = L^{-2}\Delta_2'$. However, Δ_0 yields zero when operating on M^{CS} terms so that up to the leading order in L^{-1} we have

$$\Delta = \begin{cases} L^{-1}\Delta_1' & \text{when operating on } M^{CS} \\ \Delta_0' & \text{when operating on } M^{NS} . \end{cases} \tag{4.8}$$

(b) The scaling of the coefficients $W_\alpha^{(n)}$ in Eq. (4.2a) will depend on n; i.e.,

$$W_\alpha^{(n)\prime}(\vec{r}_1, t, \lambda) = L^{-x_{\alpha n}} W_\alpha^{(n)\prime}(\vec{r}_1', t', \lambda') . \tag{4.9}$$

As in Sec. III we expect (and justify in retrospect via self-consistency)

$$x_{01} = 1 , \quad x_{\alpha 1} = 2 \quad (\alpha \neq 0) . \tag{4.10}$$

However for $n > 1$ the coefficients $W^{(n)}$ are related to products of coefficients of lower order. We therefore expect

$$x_{\alpha n} \geq n \quad (\alpha = 0, 1, \ldots ; \; n > 1) .$$

With these modifications the scaling procedure is essentially as in Sec. III. We find that the choices

$$z = y = 2, \quad x_{01} = 1, \quad x_{02} = x_{\alpha 1} = x_{\alpha 2} = 2 \tag{4.11}$$

lead to a consistent set of scaled equations. Equation (4.1a) yields in order L^{-2}

$$\sum_{\alpha \neq 0} D_{0\alpha} \Delta' M_\alpha'^{NS} = 0 , \tag{4.12a}$$

where

$$D_{\alpha\alpha'} \equiv \langle \alpha 0 k_c^2 | \underline{\underline{D}} | \alpha' 0 k_c^2 \rangle , \tag{4.12b}$$

while terms which scale like L^{-3} are related by the equation

$$\frac{\partial M_0'^{CS}}{\partial t'} = \bar{\gamma}_0 \lambda' M_0'^{CS} + \sum_{\alpha=0} D_{0\alpha} \Delta' M_\alpha'^{CS} + 2 \sum_{\alpha=0} \bar{N}_{0\alpha}^0(0) (M_0'^{CS} M_\alpha')^{CS} , \tag{4.13}$$

where $\bar{\gamma}_0$ is the coefficient of λ in the leading term of the λ expansion of $\gamma_0(\lambda, k_c^2)$.

Turning now to (4.1b) we find that the leading terms are $O(L^{-2})$ and to this order

$$0 = D_{\alpha 0} \Delta' M_0' + \sum_{\alpha' \neq 0} D_{\alpha\alpha'} \Delta' M_\alpha' + \gamma_\alpha(0, k_c^2) M_\alpha' + \bar{N}_{00}^\alpha(0) M_0'^2 \quad (\alpha \neq 0) . \tag{4.14}$$

The following comments should clarify the nature of Eqs. (4.12–14)

(a) The operator Δ' appearing in these equations is defined differently when it operates on CS or on NS functions

$$\Delta'\begin{pmatrix} M^{\mathrm{CS}} \\ M^{\mathrm{NS}} \end{pmatrix} \equiv \begin{pmatrix} \Delta_1' M^{\mathrm{CS}} \\ \Delta_0' M^{\mathrm{NS}} \end{pmatrix}.$$

(b) Equation (4.14) contains both CS and NS terms and can be separated into two equations. The CS equation is

$$0 = D_{\alpha 0}\Delta_1' M_0'^{\mathrm{CS}} + \gamma_\alpha(0, k_c^2) M_\alpha'^{\mathrm{CS}} + N_{00}^\alpha(0)(M_0'^2)^{\mathrm{CS}} \quad (\alpha \neq 0), \tag{4.15a}$$

while the NS terms satisfy

$$0 = \sum_{\alpha'} D_{\alpha\alpha'}\Delta_0' M_{\alpha'}'^{\mathrm{NS}} + \gamma_\alpha(0, k_c^2) M_\alpha'^{\mathrm{NS}} + N_{00}^\alpha(0)(M_0'^2)^{\mathrm{NS}} \quad (\alpha \neq 0). \tag{4.15b}$$

Both Eqs. (4.15a) and (4.15b) are obtained in order L^{-2}. The separation is achieved because each equation involves different Fourier components.

Equations (4.15) are the adiabatic-following equations which provide relations between M_α ($\alpha \neq 0$) and M_0^{CS} near the critical point. Next we invert these equations in order to explicitly obtain these relations. The primes indicating scaled variables will be omitted henceforth.

Equation (4.15a) yields

$$M_\alpha^{\mathrm{CS}} = -\frac{1}{\gamma_\alpha}\left[D_{\alpha 0}\Delta_1 M_0^{\mathrm{CS}} + N_{00}^\alpha (M_0^2)^{\mathrm{CS}}\right] \quad (\alpha \neq 0). \tag{4.16}$$

In order to invert (4.15b) we first note that (4.12) and (4.15b) may be combined to yield

$$\sum_{\alpha'} D_{\alpha\alpha'}\Delta_0 M_{\alpha'}^{\mathrm{NS}} + \gamma_\alpha(0, k_c^2) M_\alpha^{\mathrm{NS}} + N_{00}^\alpha(0)(M_0^2)^{\mathrm{NS}} = 0 \quad (\text{all } \alpha), \tag{4.17}$$

where the summation on α' includes $\alpha' = 0$. For $\alpha = 0$ (4.17) and the identities $\gamma_0(0, k_c^2)$, $N_{00}^0(0) = 0$ lead back to (4.12), while for $\alpha \neq 0$ (4.17) is identical to (4.15b). To invert (4.17) we use the identities

$$\begin{aligned} &\langle \alpha 0 k_c^2 | \underline{\underline{D}} | \alpha' 0 k_c^2 \rangle \Delta_0 + \gamma_\alpha(0, k_c^2)\delta_{\alpha\alpha'} \\ &\quad = \langle \alpha 0 k_c^2 | \underline{\underline{D}}\Delta_0 + \underline{\underline{\Omega}}_0 - \underline{\underline{D}} k_c^2 | \alpha' 0 k_c^2 \rangle \\ &\quad = \langle \alpha 0 k_c^2 | \underline{\underline{\Omega}}_0 + \underline{\underline{D}}\nabla_0^2 | \alpha' 0 k_0^2 \rangle, \end{aligned}$$

and obtain

$$M_\alpha^{\mathrm{NS}} = -\sum_{\alpha' \neq 0} \langle \alpha 0 k_c^2 | (\underline{\underline{\Omega}}_0 + \underline{\underline{D}}\nabla_0^2)^{-1} | \alpha' 0 k_c^2 \rangle N_{00}^{\alpha'} (M_0^2)^{\mathrm{NS}}. \tag{4.18}$$

This equation holds for all α, however only the $\alpha \neq 0$ information is needed. Inserting Eqs. (4.16) and (4.18) into (4.13) we obtain after some algebra

$$\begin{aligned} \frac{\partial M_0}{\partial t} = \bar{\gamma}_0 \lambda M_0 &- \langle 00k_c^2 | \underline{\underline{D}}(\Omega_0 - \underline{\underline{D}} k_c^2)^{-1} \underline{\underline{D}} | 00k_c^2 \rangle (\Delta_1)^2 M_0 \\ &- \langle 00k_c^2 | \underline{\underline{D}}(\underline{\underline{\Omega}}_0 - \underline{\underline{D}} k_c^2)^{-1} | v_1 \rangle \Delta_1 (M_0^2) \\ &- 2M_0 \langle 00k_c^2 | \underline{\underline{\underline{N}}}_2 : | 00k_c^2 \rangle | v_2 \rangle \Delta_1 M_0 \\ &- 2M_0 \langle 00k_c^2 | \underline{\underline{\underline{N}}}_2 : | 00k_c^2 \rangle | v_3^{\mathrm{op}} \rangle M_0^2, \end{aligned} \tag{4.19}$$

where all the M_0's are CS functions and where

$$| v_1 \rangle \equiv \underline{\underline{\underline{N}}}_2 : | 00k_c^2 \rangle | 00k_c^2 \rangle, \tag{4.20a}$$

$$| v_2 \rangle \equiv (\underline{\underline{\Omega}}_0 - \underline{\underline{D}} k_c^2)^{-1} \underline{\underline{D}} | 00k_c^2 \rangle, \tag{4.20b}$$

$$| v_3^{\mathrm{op}} \rangle \equiv (\underline{\underline{\Omega}}_0 + \underline{\underline{D}}\nabla_0^2)^{-1} \underline{\underline{\underline{N}}}_2 : | 00k_c^2 \rangle | 00k_c^2 \rangle. \tag{4.20c}$$

Note that the derivative operator in $| v_3^{\mathrm{op}} \rangle$ operates on the M_0 functions appearing on its right. Also note that indeed the operators $(\Omega_0 - \underline{\underline{D}} k_c^2)^{-1}$ and $(\underline{\underline{\Omega}}_0 - \underline{\underline{D}}\nabla_0^2)^{-1}$ operate only on vectors orthogonal to $| 00k_c^2 \rangle$, which is the null vector of the matrix $\underline{\underline{\Omega}}_0 - \underline{\underline{D}} k_c^2$. This is seen from Eqs. (2.25) and (2.38), and hence all terms are well defined.

Equation (4.19) constitutes the final formal result of the scaling procedure. This is an equation of motion for the critical mode amplitude M_0 which plays the role of a Ginzburg-Landau equation. A more explicit form is obtained by expanding M_0 in the form

$$M_0 = \sum_I W_I(\vec{r}_1) \exp(i \vec{k}_c^I \cdot \vec{r}_0),$$

and using (4.7). This leads to a Ginzburg Landau equation for the amplitudes W_I

$$\begin{aligned} \frac{\partial W_J}{\partial t} = \bar{\gamma}_0 \lambda W_J &+ 4 \langle 00k_c^2 | \underline{\underline{D}}(\underline{\underline{\Omega}}_0 - \underline{\underline{D}} k_c^2)^{-1} \underline{\underline{D}} | 00k_c^2 \rangle [(\vec{k}_c^J \cdot \vec{\nabla}_1)^2 W_J] - 2i \langle 00k_0^2 | \underline{\underline{D}}(\underline{\underline{\Omega}}_0 - \underline{\underline{D}} k_c^2)^{-1} | v_1 \rangle \sum_I \vec{k}_c^J \cdot \vec{\nabla}_1 (W_I W_{I(J)}) \\ &- 4i \langle 00k_c^2 | \underline{\underline{\underline{N}}} : | 00k_c^2 \rangle | v_2 \rangle \sum_I W_{I(J)} \vec{k}_c^I \cdot \vec{\nabla}_1 W_I - 2 \sum_{II'I''} \delta(\vec{k}_c^I + \vec{k}_c^{I'} + \vec{k}_c^{I''}, \vec{k}_c^J) \langle 00k_c^2 | \underline{\underline{\underline{N}}}_2 : | 00k_c^2 \rangle | v_3^{II'} \rangle W_I W_{I'} W_{I''} \end{aligned} \tag{4.21}$$

where $I(J)$ is a direction defined such that $\vec{I} + \vec{I}(J) = \vec{J}$, where $\vec{I}$, $\vec{I}(J)$, and $\vec{J}$ are unit vectors in the corresponding directions; $\delta(a, b)$ is the Kroncker delta; and $| v_1 \rangle$, $| v_2 \rangle$, and $| v_3^{II'} \rangle$ are defined in Eqs. (A37)–(A39). The result (4.21) agrees with the corresponding result (A31)–(A39), obtained in Appendix A using a standard bifurcation analysis, provided that the identity

$$\bar{\gamma}_0 = \langle 00k_c^2 | \underline{\underline{\Omega}}_1 | 00k_c^2 \rangle \tag{4.22}$$

holds, where Ω_1 is defined by (A3). (λ' is identical to λ_2 defined in Appendix A.) Indeed (4.22) is just the perturbation theoretic expression for the $O(\lambda)$ term in $\gamma_0(\lambda, k_c^2)$.

Equation (4.21) yields the special case of dimensionality 1 by noting that the two terms containing $W_I W_{I(J)}$ cannot appear for this dimensionality. Equation (4.21) then becomes identical to (A11).

We end this section with the following comments.

(a) The derivation did not involve any assumptions about the dimensionality of the system or about the emerging structure. We did assume however that for a given d-dimensional structure all the d spatial directions are equivalent. Our procedure has to be modified somewhat in cases where alternate scaling has to be applied in different spatial directions (as for the horizontal and the vertical directions in the roll formation of the convective instability). In particular we shall show that this must be done in the presence of electric fields in reacting systems with ionic species.[11]

(b) A striking difference between the present results, Eqs. (4.19) and (4.21), and the homogeneous case is the appearance here of transport terms which are nonlinear (quadratic) in the order parameter. Such terms do not appear for $d=1$. This can be realized by noting that in one dimension, terms quadratic in M_0 will correspond to either $k\sim 0$ or $k\sim 2k_c$ structures and will therefore be irrelevant under the scaling. The one-dimensional symmetry-breaking case is studied in detail in Appendix A and in Refs. 1 and 2.

(c) Another important difference between the results obtained here [Eq. (4.21)] and the homogeneous case lies in the appearance of coupled order parameters corresponding to different directions on the critical shell. Similar situations have been noted in the Bernard instability[6] and in particular cases of equilibrium critical phenomena.[12]

V. EXTRINSIC SYMMETRY-BREAKING INSTABILITIES

The scaling approach here may be viewed as a special case of the intrinsic instability when $k_c=0$. The fact that $\gamma_0(\lambda, k^2=0)$ is always zero (see Fig. 4) leads to the special features of this case. Starting from (2.16), we obtain (3.4) and (3.5), only the term $\gamma_0 M_0$ of (3.4) now vanishes. Near the transition point D_{00} is of order λ [cf. (2.39)]. We assume that $N_{00}^0(\lambda)$ vanishes for $\lambda\to 0$ as in the homogeneous case [see discussion preceding Eq. (3.8)]. We thus have for the scaling (2.1)

$$D_{00}=L^{-y}D'_{00}\,, \quad N_{00}^0=L^{-w}N_{00}^{0\prime} \quad (w, y>0)\,. \tag{5.1}$$

After scaling, the equation for the critical-mode amplitude takes the form

$$\begin{aligned}\frac{\partial M'_0}{\partial t'}=&L^{z-y-2}D'_{00}\nabla'^2 M'_0+L^{z-w-x_0}N_{00}^{0\prime}M_0'^2\\&+2\sum_{\alpha\neq 0}L^{z-x_\alpha}N_{0\alpha}^0 M'_0 M'_\alpha\\&+L^{z+x_0-2}\sum_{\alpha\neq 0}L^{-x_\alpha}D_{0\alpha}\nabla'^2 M'_\alpha\\&+L^{z+x_0}\sum_{\alpha,\alpha'\neq 0}L^{-x_\alpha-x_{\alpha'}}N_{\alpha\alpha'}^0 M'_\alpha M'_{\alpha'}\,,\end{aligned} \tag{5.2}$$

while the equations for the noncritical amplitudes are identical to Eq. (3.11). Equation (5.2) suggests the following scaling relations:

$$z=x_\alpha=y+2=2+x_\alpha-x_0\leqslant w+x_0\,. \tag{5.3}$$

As in (3.10), the M_0^2 term is relevant only if $z=w+x_0$ and will be irrelevant if the inequality holds. The last term of (5.2) is irrelevant. Equation (3.11) again suggests that $x_\alpha=2x_0$, and we obtain

$$x_0=y=2\,, \quad x_\alpha=z=4\,, \quad \alpha\neq 0\,. \tag{5.4}$$

Equation (3.11) then leads to

$$M'_\alpha=-N_{00}^\alpha M_0'^2/\gamma'_\alpha\,, \tag{5.5}$$

and insertion into the relevant part of (5.2) yields

$$\begin{aligned}\frac{\partial M'_0}{\partial t}=&D'_{00}\nabla'^2 M'_0+2\sum_{\alpha\neq 0}\frac{N_{0\alpha}^0 N_{00}^\alpha}{\gamma_\alpha}M_0'^3\\&-\sum_{\alpha\neq 0}\frac{D_{0\alpha}N_{00}^\alpha}{\gamma_\alpha}\nabla'^2(M_0^2)\quad(+N_{00}^{0\prime}M_0'^2)\,.\end{aligned} \tag{5.6}$$

The bracketed $M_0'^2$ term appears only if $w=2$. For this scaling to be correct we must have $w\geqslant 2$. Hence $N_{00}^0(\lambda)$ must vanish at least as fast as λ as $\lambda\to 0$.

As in the intrinsic symmetry-breaking case, we again encounter a nonlinear transport term. Redefining coefficients in an obvious way we rewrite (5.6) for the case $w>2$ as

$$\frac{\partial m}{\partial t}=(e+bm)\nabla^2 m+c|\vec{\nabla}m|^2-am^3\,.$$

As the system is driven to instability e drops below zero and the diffusion term tends to amplify pattern. Eventually this may be balanced off by the b and c terms (according to their signs) and by the cubic term (which must, for globally stable systems, imply $a>0$).

VI. FLUCTUATIONS AND THE GINZBURG CRITERION

In this section we extend the scaling procedure to include fluctuations within the Langevin formalism. As was pointed out in previous work,[13] the application of the Langevin equation near a critical point should be carried out with caution. Its simple-minded use is justified only under conditions which ensure small fluctuations (i.e., far enough from the critical point). Even if it is assumed that the Langevin representation is a good starting point, its utilization in the close vicinity of the critical point requires a major modification of the scaling procedure described in the present paper. However as we shall see, the present scaling procedure (which may be termed mean-field-type scaling) is capable of predicting its own limit of validity and therefore to yield in a straightforward way generalized Ginzburg criteria which estimate, for every case considered, the size of the critical region within which mean-field theory and mean-field-type scaling are expected to fail. This application of the scaling procedure has already been demonstrated by one of us for the homogeneous case.[3]

In Appendix B we demonstrate the application of mean-field scaling for the derivation of the Ginzburg criterion for the standard time-dependent Ginzburg–Landau model. In what follows we consider first homogeneous transitions of the kind considered in Sec. III and then symmetry-breaking transitions as discussed in Sec. IV.

A. Homogeneous transitions

Starting with (2.12), we assume that fluctuations from the mean behavior can be incorporated by introducing Langevin noise sources into the kinetic equations. In principle one should distinguish between two types of noise terms, i.e., those corresponding to conservative processes and those arising from nonconservative processes. Terms of the first kind are described by adding fluctuating terms to the currents of the state variables, while those of the second kind by adding fluctuating terms as in homogeneous contributions to the time derivatives $\partial \underline{C}/\partial t$. With this procedure (2.12) becomes

$$\frac{\partial \underline{C}}{\partial t} = \underline{\underline{D}}\nabla^2 \underline{C} + \underline{\underline{\Omega}}(\lambda)\underline{C} + \underline{\underline{N}}_2 : \underline{C}\,\underline{C} + \ldots + \underline{f}(\vec{r}, t)\,, \tag{6.1}$$

with

$$\underline{f}(\vec{r}, t) = \underline{f}_D(\vec{r}, t) + \underline{f}_R(\vec{r}, t)\,, \tag{6.2}$$

where $\underline{f}_D$ stands for the conservative and $\underline{f}_R$ for the nonconservative random noises. In the simplest model involving Gaussian, δ-correlated noise sources these terms satisfy[14]

$$\langle \underline{f}_D \underline{f}_R \rangle = \langle \underline{f}_D \rangle = \langle \underline{f}_R \rangle = 0\,, \tag{6.3}$$

$$\langle \underline{f}_D(\vec{r}, t)\underline{f}_D(\vec{r}_a, t_a)\rangle = \vec{\nabla}\cdot\vec{\nabla}_a \delta(\vec{r} - \vec{r}_a)\delta(t - t_a)\underline{\underline{S}}\,, \tag{6.4a}$$

$$\langle \underline{f}_R(\vec{r}, t)\underline{f}_R(\vec{r}_a, t_a)\rangle = \delta(\vec{r} - \vec{r}_a)\delta(t - t_a)\underline{\underline{Q}}\,. \tag{6.4b}$$

The form (6.4) assumes that the reference (mean) state is homogeneous; $\underline{\underline{S}}$ and $\underline{\underline{Q}}$ are matrices depending on the mean properties of the system. In the typical case where the dynamics of the system is governed by chemical reactions and diffusion processes, the matrices $\underline{\underline{S}}$ and $\underline{\underline{Q}}$ near a steady state have been shown[3,14] to take the forms

$$S_{ij} = (2D_j M_j C_j^0/A_0)\delta_{ij}\,, \tag{6.5}$$

$$Q_{ij} = \sum_R \nu_{iR}\nu_{jR}\frac{\mathfrak{M}_i \mathfrak{M}_j}{A_0}(r_{fR}^0 + r_{bR}^0)\,, \tag{6.6}$$

where C_j^0 are the steady-state concentrations of the different components, D_j are their diffusion coefficients (the diffusion matrix is assumed to be diagonal), $\mathfrak{M}_j$ are their molecular weights, ν_{jR} are the corresponding stochiometric coefficients in the reaction R, r_{fR}^0 and r_{bR}^0 are the forward and backward steady-state rates of the reaction R, and, finally, A_0 is the Avogadro number.

In what follows we shall assume that (6.1) has been made dimensionless[15] by defining all quantities in terms of their typical values. Examples of such a procedure are described in Appendix B and in Ref. 3. Proceeding as in Sec. III, Eqs. (3.4) and (3.5) are now replaced by

$$\begin{aligned}\frac{\partial M_0}{\partial t} = {} & D_{00}\nabla^2 M_0 + \gamma_0 M_0 + N_{00}^0 M_0^2 + 2\sum_{\alpha\neq 0} N_{0\alpha}^0 M_0 M_\alpha \\ & + \sum_{\alpha\neq 0} D_{0\alpha}\nabla^2 M_\alpha + \sum_{\alpha,\alpha'\neq 0} N_{\alpha\alpha'}^0 M_\alpha M_{\alpha'} \\ & + \langle 0\lambda | f_D\rangle + \langle 0\lambda | f_R\rangle\,,\end{aligned} \tag{6.7}$$

$$\begin{aligned}\frac{\partial M_\alpha}{\partial t} = {} & D_{\alpha 0}\nabla^2 M_0 + \sum_{\beta\neq 0} D_{\alpha\beta}\nabla^2 M_\beta + \gamma_\alpha M_\alpha \\ & + 2\sum_{\beta\neq 0} N_{0\beta}^\alpha M_0 M_\beta + \sum_{\beta,\beta'\neq 0} N_{\beta\beta'}^\alpha M_\beta M_{\beta'} + N_{00}^\alpha M_0^2 \\ & + \langle \alpha\lambda | f_D\rangle + \langle \alpha\lambda | f_R\rangle\,.\end{aligned} \tag{6.8}$$

The scaling procedure is now repeated exactly as in Sec. III. We note that, with the choice of scaling exponents as was made in Sec. III, we have

$$\begin{aligned}&\delta(\vec{r} - \vec{r}_a)\delta(t - t_a) = L^{-d-2}\delta(\vec{r}\,' - \vec{r}_a')\delta(t' - t_a')\,, \\ &\vec{\nabla}\cdot\vec{\nabla}_a = L^{-2}\vec{\nabla}'\cdot\vec{\nabla}_a'\,.\end{aligned} \tag{6.9}$$

If we further assume

$$\underline{\underline{S}} = L^{-2\varphi_D}\underline{\underline{S}}'\,, \quad \underline{\underline{Q}} = L^{-2\varphi_R}\underline{\underline{Q}}' \tag{6.10}$$

[the usual choice is $\varphi_D = \varphi_R = 0$; see Ref. 7(b) for a different case], we obtain

$$\begin{aligned}&\underline{f}_D(\vec{r}, t) = L^{-(d+4)/2-\varphi_D} f_D'(\vec{r}\,', t')\,, \\ &\underline{f}_R(\vec{r}, t) = L^{-(d+2)/2-\varphi_R} f_R'(\vec{r}\,', t')\,.\end{aligned} \tag{6.11}$$

Equations (6.7) and (6.8) then yield after scaling

$$\frac{\partial M_0'}{\partial t'} = D_{00}\nabla'^2 M_0' + \gamma_0' M_0' + 2\sum_{\alpha\neq 0} N_{0\alpha}^{0\prime} M_0' M_\alpha' \quad (+N_{00}^{0\prime} M_0^2),$$
$$+ L^{-(d-2)/2-\varphi_D}\langle 00|f_D'\rangle + L^{-(d-4)/2-\varphi_R}\langle 00|f_R'\rangle, \tag{6.12}$$

$$\gamma_\alpha M_\alpha' + N_{00}^\alpha M_0'^2 + L^{-d/2-\varphi_D}\langle \alpha 0|f_D'\rangle$$
$$+ L^{-(d-2)/2-\varphi_R}\langle \alpha 0|f_R'\rangle = 0 \quad (\alpha\neq 0). \tag{6.13}$$

The bracketed term in (6.12) has the same status as discussed in Sec. III [c.f. (3.15)]. Assuming that $\varphi_D=\varphi_R=0$, we see that the fluctuating term in (6.13) vanishes for $d>2$ as $L\to\infty$. Equation (6.13) therefore yields for $d>2$

$$M_\alpha' = -(N_{00}^\alpha/\gamma_\alpha) M_0'^2 \quad (\alpha\neq 0), \tag{6.14}$$

which is identical to (3.13). Similarly the f_D term in (6.12) is much smaller than the f_R term near the critical point and may be disregarded (a detailed discussion of this point is provided in Ref. 3). Equations (6.12) and (6.14) then lead to the equation

$$\frac{\partial M_0}{\partial t} = D_{00}\nabla^2 M_0 + \gamma_0 M_0$$
$$-2\left(\sum_{\alpha\neq 0}\frac{|N_{0\alpha}^0 N_{00}^\alpha|}{\gamma_0}\right) M_0^3 \quad (+N_{00}^0 M_0^2) + f_{00}(\vec{r},t), \tag{6.15}$$

where

$$f_{00}(r,t) = L^{-(d-4)/2}\langle 00|f_R'\rangle, \tag{6.16}$$

and where we have omitted the primes denoting scaled variables [except in (6.16) for special emphasis]. The result (6.15) is valid only provided the strength $\Phi^{1/2}$ of the random-noise term defined by

$$\langle f_{00}(r,t) f_{00}(r_a,t_a)\rangle = \Phi\delta(r-r_a)\delta(t-t_a), \tag{6.17}$$

is of order less than or equal to that of the other terms in (6.15). Since we work in dimensionless units all these scaled terms are $O(1)$, and hence noise will not dominate the equations, e.g. change the scaling, if $\Phi\lesssim 1$. From (6.4) and (6.16), we have

$$\Phi = L^{-(d-4)}\langle 00|\underline{\underline{Q}}|00\rangle \equiv L^{-(d-4)}\tilde{\Phi}. \tag{6.18}$$

Thus the condition for the validity of (6.15) becomes

$$\tilde{\Phi}\lesssim L^{d-4}. \tag{6.19}$$

As is demonstrated in Appendix B, this is just the scaled dimensionless form of the Ginzburg criterion for the distance (determined by $\lambda\sim L^{-2}$) from the critical point below which mean-field theory fails. The present scaling procedure (as well as other perturbative derivations of TDGL equations for bifurcation phenomena) fails under the same condition. To obtain this criterion in a more physical form, we have to go to the dimensional representation which depends on the particular problem studied. Thus for example, rewriting Eq. (6.19) in the form

$$\langle 00|\underline{\underline{Q}}|00\rangle \lesssim \lambda^{(4-d)/2},$$

taking λ to correspond to the feeding rate of some chemical component, and recalling that $\underline{\underline{Q}}$ arises from chemical fluctuations, we obtain[3]

$$\langle 00|\underline{\underline{Q}}|00\rangle \simeq \frac{\mathfrak{M}}{A_0}\frac{(\delta\theta)^{-d/2}}{\gamma},$$
$$\lambda\sim\Lambda\frac{\theta}{\gamma}.$$

Here $\mathfrak{M}$ is a typical molecular weight; A_0, the Avogadro number; Λ the feeding rate expressed in units of mass/(time × volume) (Λ actually expresses the deviation of the feeding rate from its critical value); and δ, θ, and γ are, respectively, characteristic diffusion coefficient, time, and concentration. The dimensioned form of the Ginzburg criterion then takes the form

$$\Lambda^{(4-d)/2} \gtrsim \frac{\mathfrak{M}\gamma}{A_0\theta^2(\delta\gamma)^{d/2}}. \tag{6.20}$$

This relation was investigated in Ref. 3 with the conclusion that breakdown of mean-field theory is in principle possible for chemically reacting and diffusing systems.

Two more comments should be made at this point. First, note that for $d>4$ the condition (6.19) is always satisfied whereas for $d<4$ the condition becomes increasingly restrictive, e.g., the Ginzburg region wherein nonclassical (non-mean-field) behavior is found becomes increasingly wide. This suggests that nonclassical behavior may be more readily found in say two-dimensional reacting media (such as thin layers) than in three-dimensional reaction volumes. The critical dimensionality for homogeneous steady-state bifurcations (dimensionality above which mean-field theory is valid arbitrarily close to the bifurcation point) is seen to be four. We shall find other values of the critical dimensionality for different types of transitions.

Second, we have seen that conservative fluctuations do not affect the Ginzburg criterion for the case of homogeneous transitions. Different behavior will be found for intrinsic symmetry-breaking transitions.

B. Intrinsic symmetry-breaking transitions

We start again with the dimensionless kinetic equation written now in the form (summation over repeated indices is implied)

$$\frac{\partial \underline{C}}{\partial t} = \underline{\underline{D}}\nabla^2 \underline{C} + \underline{\underline{\Omega}}(\lambda)\underline{C} + \underline{\underline{\underline{N}}}_2 : \underline{C}\underline{C} + \cdots + \partial_j \underline{s}^j + \underline{f}_R ; \tag{6.21}$$

because of reasons made clear below we have written the conservative fluctuating term f_D as a divergence of a current term $\vec{\underline{s}}$. We denote

$$\vec{\underline{s}} \equiv (\underline{s}^1, \underline{s}^2, \ldots, \underline{s}^d),$$

where $\underline{s}^j$ is the jth spatial component of the current vector and it is a vector in the component space (s_α^j is the jth spatial component of the current of species α). Again $\underline{f}_R$ satisfied (4.4a) while for s^j we have

$$\langle s^j(\vec{r}, t) s^k(\vec{r}_a, t_a)\rangle = \delta(\vec{r} - \vec{r}_a)\delta(t - t_a)\delta_{jk}\underline{S} \tag{6.22}$$

and

$$\partial_j \underline{s}^j = \underline{f}_D . \tag{6.23}$$

Equations (6.22, 23) are easily seen to imply (6.4a).

We are interested in fluctuations around a reference state with a spatial structure corresponding to wave vectors of magnitude k_c. For this purpose we write $\underline{f}_R$ and $\underline{s}^j$ in the form

$$\underline{f}_R(\vec{r}, t) = \frac{1}{\sqrt{N}} \sum_J e^{i\vec{k}_c^J \cdot \vec{r}} \underline{\varphi}_J(\vec{r}, t), \tag{6.24}$$

$$\underline{s}^j(\vec{r}, t) = \frac{1}{\sqrt{N}} \sum_J e^{i\vec{k}_c^J \cdot \vec{r}} \underline{\sigma}_J^j(\vec{r}, t), \tag{6.25}$$

where N is the number of directions J contributing to those sums and where the index J denote the direction of the vector $\vec{k}_c^J$ (cf. Appendix A. Note that $\varphi_{-J} = \varphi_J^*$, $\underline{\sigma}_{-J} = \underline{\sigma}_J^*$, and $\vec{k}_c^{-J} = -\vec{k}_c^J$). In order to be consistent with former assumptions we take

$$\langle \underline{\varphi}_J(\vec{r}, t) \underline{\varphi}_{J'}(\vec{r}_a, t_a)\rangle = \delta(\vec{r} - \vec{r}_a)\delta(t - t_a)\delta_{J,-J'}\underline{\underline{Q}}, \tag{6.26}$$

[which, using (6.24) gives (6.4b)] and

$$\langle \sigma_J^j(\vec{r}, t) \sigma_{J'}^{j'}(\vec{r}_a, t_a)\rangle = \delta(\vec{r} - \vec{r}_a)\delta(t - t_a)\delta_{J,-J'}\delta_{jj'}\underline{\underline{S}}, \tag{6.27}$$

[which, with (6.25) yields (6.22)]. We further note that [cf. (6.23) and (6.25)]

$$\underline{f}_D = \frac{1}{\sqrt{N}} \sum_J e^{i\vec{k}_c^J \cdot \vec{r}} (i\vec{k}_c^J + \vec{\nabla}) \cdot \underline{\vec{\sigma}}_J \tag{6.27a}$$

$$\cong \frac{1}{\sqrt{N}} \sum_J e^{i\vec{k}_c^J \cdot \vec{r}} i k_c^J \cdot \underline{\vec{\sigma}}_J . \tag{6.27b}$$

The approximation (6.27b) is made with the anticipation that the ∇ containing term in (6.27a) will scale with one L^{-1} factor more than the other term and can be disregarded close to the critical point. Eq. (6.27b) then yields [using (6.27)]

$$\langle \underline{f}_D(\vec{r}, t) \underline{f}_D(\vec{r}_a, t_a)\rangle = \delta(\vec{r} - \vec{r}_a)\delta(t - t_a) k_c^2 \underline{\underline{S}} . \tag{6.28}$$

Combining now (6.28), (6.23), and (6.4b), we obtain (6.21) in the form

$$\frac{\partial \underline{C}}{\partial t} = \underline{\underline{D}}\nabla^2 \underline{C} + \underline{\underline{\Omega}}(\lambda)\underline{C} + \underline{\underline{\underline{N}}}_2 : \underline{C}\,\underline{C} + \cdots + \underline{f}(\vec{r}, t), \tag{6.29}$$

where the random term satisfies

$$\begin{aligned} &\langle \underline{f}(\vec{r}, t)\rangle = 0, \\ &\langle \underline{f}(\vec{r}, t) \underline{f}(\vec{r}_a, t_a)\rangle = \delta(\vec{r} - \vec{r}_a)\delta(t - t_a)(\underline{\underline{Q}} + k_c^2 \underline{\underline{S}}) . \end{aligned} \tag{6.30}$$

In the representation based on the eigenvectors $|\alpha\lambda k_c^2\rangle$ of the matrix $\underline{\underline{\Gamma}}_0(\lambda) = \underline{\underline{\Omega}}(\lambda) - k_c^2 \underline{\underline{D}}$, (6.29) takes the form [equivalent to (2.36)].

$$\frac{\partial M_\beta}{\partial t} = \sum_\alpha \langle \beta\lambda k_c^2 | \underline{\underline{D}} | \alpha\lambda k_c^2\rangle (\nabla^2 + k_c^2) M_\alpha + \gamma_\beta(\lambda, k_c^2) M_\beta + \sum_\alpha \sum_{\alpha'} N_{\alpha\alpha'}^\beta(\lambda) M_\alpha M_{\alpha'} + \cdots + \langle \beta\lambda k_c^2 | \underline{f}(\vec{r}, t)\rangle, \tag{6.31}$$

where all the notations are as defined in Sec. II. Making the reasonable assumption that $\langle 00k_c^2 | f(\vec{r}, t)\rangle \neq 0$, the scaling procedure can be repeated along lines identical to Sec. IV. The following points should be noted with regard to this scaling procedure.

(a) The random term $\langle \beta\lambda k_c^2 | f(\vec{r}, t)\rangle$ scales like $\langle \beta 0 k_c^2 | \underline{f}(\vec{r}, t)\rangle$ as $L \to \infty$. Corrections to this scaling involve terms which are higher order in $\lambda(\sim L^{-2})$.

(b) Equations (6.24) and (6.25) imply that $\underline{f}$ of (6.30) may be written in the form

$$\underline{f}(\vec{r}, t) = \frac{1}{\sqrt{N}} \sum_J \exp(i\vec{k}_c^J \cdot \vec{r}) \underline{f}_J(\vec{r}, t), \tag{6.32}$$

with

$$\langle \underline{f}_J\rangle = \underline{0}$$

and

$$\langle \underline{f}_J(\vec{r}, t) \underline{f}_{J'}(\vec{r}_a, t_a)\rangle = \delta(\vec{r} - \vec{r}_a)\delta(t - t_a)\delta_{J,-J'}(\underline{\underline{Q}} + k_c^2 \underline{\underline{S}}) . \tag{6.33}$$

In Eq. (6.32), the $f_J(\vec{r}, t)$ play the role of noise sources for fluctuations around the structure determined by the wave vectors $\vec{k}_c^J$. In the spirit of Sec. IV we rewrite Eq. (6.32) in the form

$$\underline{f}(\vec{r}, t) = \frac{1}{\sqrt{N}} \sum_J \exp(i\vec{k}_c^J \cdot \vec{r}_0) \underline{f}_J(\vec{r}_1, t) . \tag{6.34a}$$

The scaling ansatz of Sec. IV

$$\underline{f}_J(\vec{r}_1, t) = \underline{f}_J(L\vec{r}_1', L^2 t'), \tag{6.34b}$$

implies that [taking $\varphi_D = \varphi_R = 0$ in (6.10)] the scaling of $\underline{f}$ is solely determined by the $\vec{r}$ and t dependence of the δ functions of (6.30). Thus

$$\underline{f}(\vec{r}, t) = L^{-(d+2)/2} \underline{f}'(\vec{r}', t'), \tag{6.35a}$$

where

$$\underline{f}'(\vec{r}',t')=\frac{1}{\sqrt{N}}\sum_J \exp(i\vec{k}_c^J\cdot\vec{r}_0')\underline{f}_J(\vec{r}',t'). \qquad (6.35b)$$

(c) As in (6.13) the random terms in the equations for the noncritical modes are scaled out for $d>2$.

The scaling procedure now yields for the time evolution of the order parameter M_0 an equation identical to (4.19) with an additional random term in the right-hand side of the form

$$f_{00}(\vec{r},t)\equiv L^{-(d-4)/2}\langle 00k_c|f(\vec{r},t)\rangle, \qquad (6.36)$$

which is essentially equivalent to the (6.16) of the homogeneous case. Also (6.17) remains valid with Φ now given by

$$\Phi=L^{-(d-4)}\langle 00k_c|(\underline{\underline{Q}}+k_c^2\underline{\underline{S}})|00k_c\rangle\equiv L^{-(d-4)}\tilde{\Phi}. \qquad (6.37)$$

With this new definition of $\tilde{\Phi}$ the generalized Ginzburg criterion remains of the form

$$\tilde{\Phi}\lesssim\lambda^{(d-4)/2}. \qquad (6.38)$$

It should be noted that unlike the homogeneous case, here the conservative fluctuations do not scale away and make a contribution to the magnitude of $\tilde{\Phi}$.

C. Extrinsic symmetry-breaking transitions

The analysis of this case proceeds essentially as that for either the homogeneous case or the intrinsic case in the proper limit as $k_c^2\to 0$. One finds that in the presence of fluctuations using the scaling described in Sec. V [see (5.4)] the EOM (5.2) must be augmented by two terms analogous to the last two terms in (6.12), namely,

$$L^{-(d-4)/2-\varphi_D}\langle 000|f_D'\rangle+L^{-(d-6)/2-\varphi_R}\langle 000|f_R'\rangle. \qquad (6.39)$$

Using the same arguments as in Sec. VI.A we find that the diffusion (conserved) fluctuations do not contribute in the critical regime in the same order as the reactive fluctuations and are scaled out. Furthermore the Ginzburg criterion analogous to (6.20) becomes

$$\Phi\lesssim L^{d-6}.$$

Hence the critical dimensionality is six for the extrinsic case. This presents the interesting possibility that the nonclassical domain may be more easily accessible for these systems.

To end this section we summarize the assumptions made and the significance of the results obtained here. The following assumptions underline the present treatment.

(i) A Langevin equation is used as a model for fluctuations in the nonlinear system. Far enough from the critical point this description is essentially equivalent to the more general master-equation model. The question concerning the validity of the Langevin equation in the vicinity of the critical point is not addressed here as the scaling procedure itself ceases to be valid in the nonclassical critical region.

(ii) The scaling of all the parameters appearing in the kinetic equations was chosen as in Secs. III and IV. The scaling of the random forces was assumed to be determined by its $\vec{r}$ and t dependence as appear in equations like (6.4) and (6.30). Phase factors corresponding to structure like in (6.32) behave as discussed in Sec. IV.

(iii) The scaling procedure is valid near the critical point where we may distinguish between terms by their different order in L^{-1}. However, we have seen that, in the presence of fluctuations, the particular scaling applied here fails too close to the critical point, when (6.38) ceases to hold. Thus our procedure is limited to a region near the critical point but not quite at it, and there is an underlying assumption that such a mean-field scaling region exists. Estimates made for chemical and hydrodynamical systems indicate that the true critical region [in the sense of (6.38)] is in most cases extremely small so that mean-field scaling as applied in the present work is a relevant procedure.

(iv) Finally, we stress again the importance of the critical conditions [(2.7), (2.33), (2.38), etc.] in fixing the location of the critical point and in determining the details of the scaling procedure.

With these assumptions the scaling procedure was shown to yield first, a generalized time-dependent Ginzburg-Landau-Langevin equation for the order parameter M_0 characterizing the transition, and second, a generalized Ginzburg criterion which estimates both the validity of mean-field theory (or the Gaussian approximation) and the validity of the scaling procedure itself. The critical dimensionality obtained for both the homogeneous and the symmetry-breaking case is 4 for $d>4$ mean-field theory and mean-field scaling are valid for any distance from the critical point. For $d<4$ breakdown of mean-field theory and "non classical" behavior is in principle possible. A critical dimensionality 4 is seen to be a typical feature as in equilibrium phenomena. Other cases analogous to multicritical equilibrium behavior with a different critical dimensionality can of course be devised. Interestingly, critical dimensionalities other than 4 can also exist in cases such as the extrinsic symmetry-breaking instability.

VII. CONCLUSIONS

In this paper we have advanced a scaling method for the reduction of a system of nonlinear rate equations near its critical point to a generalized TDGL equation for the order parameter, identified as the amplitude of the critical mode. Utilization of critical conditions turned out to be essential for a proper reduction.

For homogeneous transitions in multiple-state systems, we obtained a TDGL equation of the common type. For intrinsic symmetry-breaking transitions (where a finite-wavelength structure appears at the transition point), we obtained coupled EDGL equations for order parameters corresponding to critical waves in different directions. For both the intrinsic and the extrinsic symmetry-breaking transitions the generalized TDGL equations contain also nonlinear diffusion terms.

The scaling procedure applied in the present paper is essentially a mean-field-type approach, and the exponents obtained are mean-field exponents. By comparing the behavior under scaling of the stochastic and the deterministic terms in the kinetic equations we were also able to obtain generalized Ginzburg criteria for the size of the nonclassical critical region. The behavior of the system inside the nonclassical region is beyond the scope of the present work. It is interesting to note that the many coupled order parameters case have been conjectured[6,12] to have a first-order transition inside the nonclassical region. However the equations studied in that case did not contain nonlinear diffusion terms.[16]

Another question of interest is the applicability of the Langevin equation near the critical point. It would be useful to develop a scaling procedure or a full renormalization equation which is a more fundamental starting point than the Langevin approach.

It should be interesting to look for critical exponents and the breakdown of mean-field theory for a system exhibiting chemical instabilities. Estimates of the critical region indicate that it is in principle accessibly for such systems. However, currently known systems seem to be not very suitable. Small diffusion coefficients, fast reactions, and a good control of the external parameters are the necessary requirements.

Estimates of the Ginzburg region for chemical phenomena of various other types (oscillations, wave, chaotic evolution) are in progress. Such a program of investigation is necessary in planning for experiments in fluctuation spectroscopy aimed at determining nonclassical critical exponents.

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APPENDIX A: BIFURCATION OF STATIC STRUCTURES

Here we outline the bifurcation analysis for intrinsic and extrinsic symmetry-breaking transitions. We limit ourselves to the static case and set all time derivatives to zero.

A. Intrinsic case for $d=1$

Consider the equation

$$\left(\underline{\underline{D}}\frac{d^2}{dx^2}+\underline{\underline{\Omega}}(\lambda)\right)\underline{C}+\underline{N}(\underline{C},\lambda)=0\,. \tag{A1}$$

For simplicity we assume that the nonlinear term $\underline{N}(\underline{C},\lambda)$ is quadratic in the deviations $\underline{C}$ from the steady state [so that (2.13) is exact without the missing terms]. This is the case in most practical examples and including higher order terms can be done without any additional difficulty. Letting ϵ be a parameter measuring the amplitude of the nascent structure, we introduce a multiple scale expansion

$$\underline{C}=\sum_{n=1}^{\infty}\underline{C}_n\epsilon^n\,,\quad \lambda=\sum_{n=1}^{\infty}\lambda_n\epsilon^n\,,\quad \frac{d}{dx}=\sum_{n=0}^{\infty}\frac{d}{dx_n}\,\epsilon^n\,. \tag{A2}$$

In the case of a transition between homogeneous steady states, the matrix $\underline{\underline{\Omega}}(\lambda)$ is usually a nonanalytic function of λ near the transition point

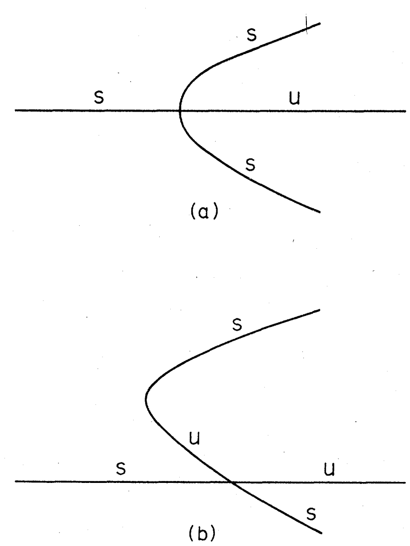

FIG. 5. Bifurcation diagrams for a second-order (critical) transition (a) and a first-order (hard) transition (b).

$\lambda=0$ [even when λ is chosen so that $\gamma_0(\lambda)$ is analytic in λ for $\lambda\to 0$]. This results from the fact that $\underline{\underline{\Omega}}'(\lambda)=\underline{\underline{\Omega}}(\underline{C}^0(\lambda),\lambda)$ and that the steady-state vector $\underline{C}^0(\lambda)$ is usually not analytic in λ for $\lambda\to 0$.[3] In the intrinsic symmetry-breaking case this is no longer so, because $\underline{\underline{\Omega}}$ depends on the homogeneous steady state, while it is the amplitude of the nonhomogeneous structure which is expected to be nonanalytic in λ. We therefore assume that $\underline{\underline{\Omega}}(\lambda)$ is analytic in λ and write

$$\underline{\underline{\Omega}}(\lambda)=\underline{\underline{\Omega}}_0+\underline{\underline{\Omega}}_1\lambda+\underline{\underline{\Omega}}_2\lambda^2+\cdots, \tag{A3}$$

where $\underline{\underline{\Omega}}_0=\underline{\underline{\Omega}}(0)$. The nonlinear part of (A1) is given by (2.13) and (2.14). We now insert the expansions (A2) into (A1) and consider the resulting equations order by order. To $O(\epsilon)$ we get

$$\left(\underline{\underline{D}}\frac{d^2}{dx_0^2}+\underline{\underline{\Omega}}_0\right)\underline{C}_1=0, \tag{A4}$$

so that

$$\underline{C}_1=[W(x_1,x_2,\ldots)e^{ik_cx_0}+W^*(x_1,x_2,\ldots)e^{-ik_cx_0}]\,|00k_c^2\rangle. \tag{A5}$$

To order ϵ^2, we obtain

$$\begin{aligned}\left(\underline{\underline{D}}\frac{d^2}{dx_0^2}+\underline{\underline{\Omega}}_0\right)\underline{C}_2&=-2\underline{\underline{D}}\frac{d^2}{dx_0dx_1}\underline{C}_1-\lambda_1\underline{\underline{\Omega}}_1\underline{C}_1-\underline{\underline{N}}_2:\underline{C}_1\underline{C}_1\\&=-2ik_c\left(\frac{dW}{dx_1}e^{ik_cx_0}-\frac{dW^*}{dx_1}e^{-ik_cx_0}\right)\underline{\underline{D}}\,|00k_c^2\rangle\\&\quad-\lambda_1(We^{ik_cx_0}+W^*e^{-ik_cx_0})\underline{\underline{\Omega}}_1\,|00k_c^2\rangle-(We^{ik_cx_0}+W^*e^{-ik_cx_0})^2\underline{\underline{N}}:|00k_c^2\rangle\,|00k_c^2\rangle.\end{aligned} \tag{A6}$$

Denoting the right hand side of (A6) by $|a(x_0,x_1,\ldots)\rangle$, the integrability condition for this equation is ($\overline{L}$ being the normalization length of our system, $\overline{L}\gg 2\pi k_c^{-1}$)

$$\frac{1}{\overline{L}}\int_{-\overline{L}/2}^{\overline{L}/2}dx_0e^{\pm ik_cx_0}\langle 00k_c^2|a(x_0,x_1,\ldots)\rangle=0. \tag{A7}$$

Using (2.25), it is easily seen that, in order to satisfy this condition, we must take $\lambda_1=0$. The solution of (A6) then becomes

$$\begin{aligned}\underline{C}_2=&-2ik_c\left(\frac{dW}{dx_1}e^{ik_cx_0}-\frac{dW^*}{dx_1}e^{-ik_cx_0}\right)(\underline{\underline{\Omega}}_0-\underline{\underline{D}}k_c^2)^{-1}\underline{\underline{D}}\,|00k_c^2\rangle-(W^2e^{2ik_cx_0}+W^{*2}e^{-2ik_cx_0})(\underline{\underline{\Omega}}_0-4\underline{\underline{D}}k_c^2)^{-1}\underline{\underline{N}}_2:|00k_c^2\rangle\,|00k_c^2\rangle\\&-2|W|^2\underline{\underline{\Omega}}_0^{-1}\underline{\underline{N}}_2:|00k_c^2\rangle\,|00k_c^2\rangle.\end{aligned} \tag{A8}$$

Turning now to order ϵ^3, we obtain

$$\left(\underline{\underline{D}}\frac{d^2}{dx_0^2}+\underline{\underline{\Omega}}_0\right)\underline{C}_3=-2\underline{\underline{D}}\frac{d^2}{dx_0dx_1}\underline{C}_2-\lambda_2\underline{\underline{\Omega}}_1\underline{C}_1+2\underline{\underline{N}}_2:\underline{C}_1\underline{C}_2-\underline{\underline{D}}\frac{d^2}{dx_1^2}\underline{C}_1, \tag{A9}$$

where we have used the expansion (A3) in the form $\underline{\underline{\Omega}}(\lambda)=\underline{\underline{\Omega}}_0+\epsilon^2\lambda_2\Omega_1+\cdots$. Eqs. (A5) and (2.25) imply that the last term on the right hand side of (A9) does not contribute to the integrability conditions which, for this equation, take the form

$$\frac{1}{\overline{L}}\int_{-\overline{L}/2}^{\overline{L}/2}dx_0e^{\pm ik_cx_0}\left\langle 00k_c^2\left|2\underline{\underline{D}}\frac{d^2}{dx_0dx_1}\underline{C}_2+\lambda_2\underline{\underline{\Omega}}_1\underline{C}_1+2\underline{\underline{N}}_2:\underline{C}_1\underline{C}_2\right.\right\rangle=0, \tag{A10}$$

fixing the value of λ_2. Because of the remaining freedom in the choice of ϵ we may choose $\lambda_2=1$ for convenience. Using (A5) and (A8), (A10) yields after some algebra

$$a_1\frac{d^2W}{dx_1^2}+a_2W+a_3W|W|^2=0, \tag{A11}$$

where

$$a_1=4k_c^2\langle 00k_c^2|\underline{\underline{D}}(\underline{\underline{\Omega}}_0-\underline{\underline{D}}k_c^2)^{-1}\underline{\underline{D}}\,|00k_c^2\rangle, \tag{A12}$$

$$a_2=\lambda_2\langle 00k_c^2|\underline{\underline{\Omega}}_1\,|00k_c^2\rangle, \tag{A13}$$

$$a_3=-2\langle 00k_c^2|\underline{\underline{N}}_2:|00k_c^2\rangle\,|v\rangle, \tag{A14}$$

and where in the last equation $\underline{v}$ is defined by

$$|v\rangle=[(\Omega_0-4Dk_c^2)^{-1}+2\underline{\underline{\Omega}}_0^{-1}]\underline{\underline{N}}_2:|00k_c^2\rangle\,|00k_c^2\rangle. \tag{A15}$$

Equation (A11) yields a single uniform solution $W=0$ below the transition and a pair of uniform solutions $W_\pm=\pm(-a_2/a_3)^{1/2}$ above it. Hence, from the form of $\underline{C}_1$ [see (A5)] and our multiscale expansion (A2), it is clear that the structures bifurcate smoothly as λ passes through zero. Typically this corresponds to a soft transition when the new branches are stable as shown in Fig. 5a. For $d>1$ the bifurcation may lead to a hard transition as in Fig. 5b. In fact, as we shall now show, for structures with $d>1$ soft transitions take place only under very special "critical" conditions.

B. Intrinsic case for $d>1$

In repeating the expansion procedure described above for $d>1$, one finds that the second-order integrability condition is no longer automatically satisfied. The reason is that the last term of the equation equivalent to (A6) is not necessarily orthogonal to the solution of the lower-order equation [equivalent to (A5)] for $d>1$. The integrability is insured if the condition

$$\langle 00k_c^2 | \underline{\underline{N}}_2 : |00k_c^2\rangle |00k_c^2\rangle = 0 , \qquad \text{(A16)}$$

is satisfied. If this is not so we get a quadratic equation for the amplitude of the bifurcating structure from the nontrivial integrability condition at this order. This in turn implies a different scaling of the bifurcating structure: in this case it is expected to be $O(\lambda)$ rather than $O(\sqrt{\lambda})$. Therefore it is necessary to apply different expansion procedures depending on whether or not (A16) is satisfied. We now consider these two cases.

1. Equation (A16) is not satisfied

As before, we expand

$$\underline{C} = \sum_{n=1}^{\infty} \underline{C}_n \epsilon^n , \qquad \text{(A17a)}$$

$$\vec{\nabla} = \sum_{n=0}^{\infty} \vec{\nabla}_n \epsilon^n , \qquad \text{(A17b)}$$

$$\lambda = \sum_{n=1}^{\infty} \lambda_n \epsilon^n , \qquad \text{(A17c)}$$

$$\underline{\underline{\Omega}}(\lambda) = \underline{\underline{\Omega}}_0 + \underline{\underline{\Omega}}_1 \lambda + \cdots . \qquad \text{(A17d)}$$

In the lowest order $[O(\epsilon)]$, we get

$$(\underline{\underline{D}} \nabla_0^2 + \underline{\underline{\Omega}}_0) \underline{C}_1 = 0 , \qquad \text{(A18)}$$

with the general solution

$$\underline{C}_1 = \left(\sum_I W_I \exp(i \vec{k}_c^I \cdot \vec{r}_0) \right) |00k_c^2\rangle . \qquad \text{(A19)}$$

Here I denotes a particular direction in the d-dimensional space such that $|\vec{k}_c^I| = k_c$, $\vec{k}_c^{-I} = -\vec{k}_c^I$, and $W_{-I} = W_I^*$. The directions which contribute to the sum in (A19) depend on the dimensionality of the system and on the geometry of the bifurcating structure.

To the next order $[O(\epsilon^2)]$, we obtain, using (A19),

$$(\underline{\underline{D}} \nabla_0^2 + \underline{\underline{\Omega}}_0) \underline{C}_2 = -[2\underline{\underline{D}} \vec{\nabla}_0 \cdot \vec{\nabla}_1 \underline{C}_1 + \lambda_1 \underline{\underline{\Omega}}_1 \underline{C}_1 + \underline{\underline{N}}_2 : \underline{C}_1 \underline{C}_1] . \qquad \text{(A20)}$$

The integrability condition implies [using (2.25)]

$$\lambda_1 \langle 00k_c^2 | \underline{\underline{\Omega}}_1 | 00k_c^2\rangle W_I + \langle 00k_c^2 | \underline{\underline{N}}_2 : |00k_c^2\rangle |00k_c^2\rangle \sum_J W_J W_{J(I)} = 0 , \qquad \text{(A21)}$$

where $J(I)$ is the unit vector such that

$$J + J(I) = I . \qquad \text{(A22)}$$

Again we may choose $\lambda_1 = 1$ to make the definition of ϵ more precise, under the assumption that, as we shall show presently, we can find nontrivial solutions of (A21).

Equation (A21) may be put in a convenient "universal" form as follows. First we introduce the notation

$$b \equiv \langle 00k_c^2 | \underline{\underline{N}}_2 : |00k_c^2\rangle |00k_c^2\rangle \times (\langle 00k_c^2 | \underline{\underline{\Omega}}_1 | 00k_c^2\rangle)^{-1} . \qquad \text{(A23)}$$

Next, one introduces U_I such that

$$W_I = U_I / b . \qquad \text{(A24)}$$

With this we obtain the parameter-free equation

$$U_I + \sum_J U_J U_{J(I)} = 0 . \qquad \text{(A25)}$$

The quadratic equations (A25) constitute the equations mixing the amplitudes of the bifurcating structures for this case, $d>1$. Several possible geometries may be considered. Besides the one-dimensional patterns (which arise with a different scaling), one may construct hexagonal patterns by choosing the unit vectors I, $I(J)$, and J to lie on an equilateral triangle. Letting x, y, and z denote U_I, $U_{I(J)}$, and U_J, we may find solutions of (A25) satisfying

$$x + yz = 0, \quad y + xz = 0, \quad z + xy = 0 . \qquad \text{(A26)}$$

One finds six solutions as permutations of the two cases

$$(x, y, z) = (1, 1, -1), \quad (-1, -1, 1) . \qquad \text{(A27)}$$

Note that, since these solutions bifurcate linearly in λ, the new branch exists on both sides of $\lambda = 0$, and the bifurcation diagram must be qualitatively as in Fig. 5b and thus corrrsponds to a hard transition for $d>1$ except, as we shall now show, under the "critical condition" wherein (A16) and other technical conditions are satisfied.

2. Equation (A16) is satisfied

When (A16) is satisfied, we see from (A21) that λ_1 must be zero for nontrivial results ($\underline{C}_1 \neq 0$). The approprite expansion is thus similar to that in the one-dimensional case:

$$\lambda = \lambda_2 \epsilon^2 + \cdots ,$$

$$\underline{C} = \sum_{n=1}^{\infty} \epsilon^n \underline{C}_n ,$$

$$\vec{\nabla} = \sum_{n=0}^{\infty} \vec{\nabla}_n \epsilon^n ,$$

and

$$\underline{\underline{\Omega}} = \underline{\underline{\Omega}}_0 + \underline{\underline{\Omega}}_1 \lambda_2 \epsilon^2 + \cdots .$$

To order $O(\epsilon)$, we obtain (A18), and $\underline{C}_1$ takes the form (A19).

In the next order, $O(\epsilon^2)$, we get

$$(\underline{\underline{D}}\nabla_0^2+\underline{\underline{\Omega}}_0)\underline{C}_2=-2\underline{\underline{D}}\vec{\nabla}_0\cdot\vec{\nabla}_1\underline{C}_1-\underline{\underline{N}}_2:\underline{C}_1\underline{C}_1\,. \qquad \text{(A28)}$$

The integrability condition for this equation is now satisfied as an identity [as implied by (A16) and (2.25)] and in fact implies $\lambda_1=0$. Equation (A28) yields

$$\underline{C}_2=-2i\sum_I(\vec{k}_c^I\cdot\vec{\nabla}_1W_I)\exp(i\vec{k}_c^I\cdot\vec{r}_0)(\underline{\underline{\Omega}}_0-\underline{\underline{D}}k_c^2)^{-1}\underline{\underline{D}}\,|00k_c^2\rangle-\sum_{II'}W_IW_{I'}\exp[i(\vec{k}_c^I+\vec{k}_c^{I'})\vec{r}_0]$$
$$\times[\underline{\underline{\Omega}}_0-\underline{\underline{D}}(\vec{k}_c^I+\vec{k}_c^{I'})^2]^{-1}\underline{\underline{N}}_2:|00k_c^2\rangle\,|00k_c^2\rangle\,. \qquad \text{(A29)}$$

Note that both the directions I and $-I$ appear in these sums. This insures that $\underline{C}_2$ is real. The $O(\epsilon^3)$ equation is

$$(\underline{\underline{D}}\nabla_0^2+\underline{\underline{\Omega}}_0)\underline{C}_3=-2\underline{\underline{D}}\vec{\nabla}_0\cdot\vec{\nabla}_2\underline{C}_1-\underline{\underline{D}}\nabla_1^2\underline{C}_1-\lambda_2\underline{\underline{\Omega}}_1\underline{C}_1$$
$$-2\underline{\underline{D}}\vec{\nabla}_0\cdot\vec{\nabla}_1C_2-2\underline{\underline{N}}_2:\underline{C}_1\underline{C}_2\,. \qquad \text{(A30)}$$

The integrability condition in this order yields the desired equation for the amplitudes W_I. The first two terms on the right-hand side of (A30) do not contribute, and the remaining terms yield

$$AW_J+B(\vec{k}_c^J\cdot\vec{\nabla}_1)^2W_J+C_1\sum_I\vec{k}_c^J\cdot\vec{\nabla}_1(W_IW_{I(J)})$$
$$+C_2\sum_I W_{I(J)}\vec{k}_c^I\cdot\vec{\nabla}_1W_I$$
$$+\sum_{II'I''}D^J_{II'I''}W_IW_{I'}W_{I''}=0\,, \qquad \text{(A31)}$$

where

$$A=\lambda_2\langle 00k_c^2|\underline{\underline{\Omega}}_1|00k_c^2\rangle\,, \qquad \text{(A32)}$$

$$B=4\langle 00k_c^2|\underline{\underline{D}}\,|v_2\rangle\,, \qquad \text{(A33)}$$

$$C_1=-2i\langle 00k_c^2|\underline{\underline{D}}(\underline{\underline{\Omega}}_0-\underline{\underline{D}}k_c^2)^{-1}|v_1\rangle\,, \qquad \text{(A34)}$$

$$C_2=-4i\langle 00k_c^2|\underline{\underline{N}}_2:|00k_c^2\rangle\,|v_2\rangle\,, \qquad \text{(A35)}$$

$$D^J_{II'I''}=2\delta(\vec{k}_c^{I'}+\vec{k}_c^{I''},\vec{k}_c^J)$$
$$\times\langle 00k_c^2|\underline{\underline{N}}_2:|00k_c^2\rangle\,|v_3^{II'}\rangle\,, \qquad \text{(A36)}$$

$\delta(a,b)$ being a Kronecker delta, and where

$$|v_1\rangle=\underline{\underline{N}}_2:|00k_c^2\rangle\,|00k_c^2\rangle\,, \qquad \text{(A37)}$$

$$|v_2\rangle=(\underline{\underline{\Omega}}_0-\underline{\underline{D}}k_c^2)^{-1}\underline{\underline{D}}\,|00k_c^2\rangle\,, \qquad \text{(A38)}$$

$$|v_3^{II'}\rangle=[\underline{\underline{\Omega}}_0-\underline{\underline{D}}(\vec{k}_c^I+\vec{k}_c^{I'})^2]^{-1}|v_1\rangle\,. \qquad \text{(A39)}$$

The resulting reduced equation (A31) is in general complex and can be easily recast as two equations involving the real and imaginary parts of the complex amplitudes.

We have not been able to show that sufficient relations exist among the coefficients $A, B, \ldots$ in (A31) so that it may be put in a universal form in analogy to (A25). However, if we limit ourselves to cases where the W_J are independent of x_1, then we may obtain a universal form at least for certain geometries. First we note that for $d=2$ the vectors I, I', I'', and J must lie on an equilateral quadrangle and for $d=3$ the additional possibility arises that they may lie on the edges of an equilateral tetrahedron (see Fig. 6). For the equilateral tetrahedron any choices of I and I' are such that $|I+I'|=1$ and hence the numerical factor in $D^J_{II'I''}$ denoted Δ henceforth, is independent of I, I'. For the equilateral quadrangle there are two possible values $|I+I|=\sqrt{3}, 0$ and hence there are two values Δ_0 and Δ_1 for the factor in $D^J_{II'I''}$. Although a full analysis of these cases is beyond the scope of the present study we consider briefly the case $d=3$ for equilateral-tetrahedral geometry. For constant W_I solutions, we let

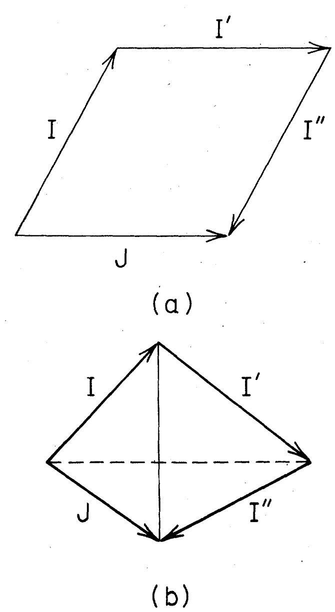

FIG. 6. Wave-vector directions of critical modes that can couple in two dimensions [case (a)] and in three or greater dimensions [case (a) or (b)] as discussed in Appendix A below Eq. (A39) for the formation of spatial patterns.

$$W_I = (A/\Delta)^{1/2} U_I \,, \tag{A40}$$

and obtain the universal equations

$$U_J + \sum_{I,I'} U_I U_{I'} U_{J-I-I'} = 0 \,. \tag{A41}$$

There are two pathways in the equilateral tetrahedron to fix I, I', I'' to get J. Let u, v, w, x, y, z denote the U_J values for the six edges of the tetrahedron. With this we obtain the coupled equations

$$\begin{aligned} &x + yuw + vuz = 0 \,, \quad y + xwu + vwz = 0 \,, \\ &z + uvx + yvw = 0 \,, \quad u + zxv + yvw = 0 \,, \\ &v + yzw + xzu = 0 \,, \quad w + uyx + vyz = 0 \,. \end{aligned} \tag{A42}$$

A particular case of these equations may be found when two of the amplitudes are zero. Taking $w = 0$ implies $y = 0$ and we have

$$\begin{aligned} &x + vuz = 0 \,, \quad z + uvx = 0 \,, \\ &u + zxv = 0 \,, \quad v + xzu = 0 \,. \end{aligned} \tag{A43}$$

This set of equations has (at least) eight solutions derivable as permutations of the cases

$$(x, z, u, v) = (1, 1, 1, -1), \ (-1, -1, -1, 1) \,. \tag{A44}$$

Thus nontrivial solutions to (A31) can clearly be found and in the present case correspond to a three-dimensional equilateral-tetrahedral array.

Note that we have demonstrated that when the condition (A16) is attained the system *may* have a soft transition. However from Fig. 7 we see that the transition may be hard in certain cases when the structure emerges as an inverted bifurcation, e.g. for $\lambda < 0$ when the null state $\underline{C} = \underline{0}$ is stable. Thus (A16) is a necessary but not sufficient condition. One more condition, as an inequality is necessary to ensure that the bifurcation will not be inverted. This condition is that guaranteeing that we may choose λ_2 positive. (Note by assumption ϵ is real so that, if we can choose $\lambda_2 > 0$, then ϵ will be real for $\lambda > 0$, e.g. not an inverted bifurcation.) We note that the solutions found in (A44) are independent of I and hence, since $W_{-I} = W_I^*$ because $\underline{C}$ is real, we must have real W_I for these solutions. Thus a further condition is, noting (A40)

$$A/\Delta > 0 \,. \tag{A45}$$

Since A is proportional to λ_2 we may thus fix the sign of λ_2, taking $\lambda_2 = \pm 1$ for convenience for the two possible cases. Ordinary eigenvalue perturbation theory shows that the coefficient of λ_2 in A [see (A32)] is just the derivative of the critical-mode eigenvalue at $\lambda = 0$, and hence, if we assume that instability is for $\lambda > 0$, then the condition for a normal (e.g. not inverted) bifurcation becomes

$$\Delta > 0 \,. \tag{A46}$$

This result has been derived for the tetrahedral patterns and is not a general result. Clearly whether a soft transition takes place at $\lambda = 0$ requires a more detailed consideration of all possible bifurcating patterns and will not be presented here.

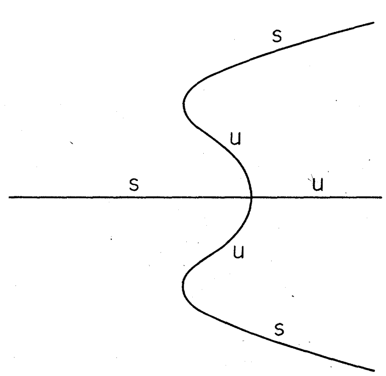

FIG. 7. Inverted bifurcation showing that the critical condition (A16) is necessary but not sufficient to guarantee a soft transition.

APPENDIX B: DERIVATION OF THE GINZBURG CRITERION FROM SCALING ARGUMENTS

Consider a Langevin equation of the form

$$\frac{\partial}{\partial t} W = D\nabla^2 W + F(W) + f(\vec{r}, t) \,, \tag{B1}$$

with f being a Gaussian random variable satisfying

$$\begin{aligned} &\langle f(\vec{r}, t)\rangle = 0 \,, \\ &\langle f(\vec{r}, t) f(\vec{r}\,', t')\rangle = \Phi\delta(\vec{r} - \vec{r}\,')\delta(t - t') \,. \end{aligned} \tag{B2}$$

Equations (B1) and (B2) correspond to the following steady-state probability distribution

$$P(W(\vec{r})) = \frac{1}{Z} \exp\left(-\frac{1}{\Phi} \int dr \{U[W(\vec{r})] + \tfrac{1}{2} D \,|\vec{\nabla} W(\vec{r})|^2\}\right), \tag{B3}$$

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

$$F(W) = -\frac{\partial U(W)}{\partial W} \,. \tag{B4}$$

For U given by

$$U(W) = \lambda W^2 + \tfrac{1}{2} \nu W^4 \,, \tag{B5}$$

the Ginzburg criterion for the validity of mean-field theory or of the Gaussian approximation (which neglects in U terms higher than quadratic in the fluctuation from the mean) is given by[17]

$$\frac{\Phi K_d \nu N}{(2\pi)^d(\frac{1}{2}D)^2}\left(\frac{\frac{1}{2}D}{\lambda}\right)^{(4-d)/2} \lesssim 1 , \tag{B6}$$

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

$$N=\int_0^\infty dx \frac{x^{d'}}{1+x^2} , \tag{B7}$$

with d' being the noninteger part of d.

Return now to (B1) written as

$$\frac{\partial}{\partial t}W = D\nabla^2 W + \lambda W + \tfrac{1}{2}\nu W^3 + f(\vec{\mathbf{r}},t) . \tag{B8}$$

It is convenient to convert (B8) into dimensionless form by expressing all quantities in terms of some characteristic values. To this end we introduce the characteristic time θ (e.g., inverse rate of some typical process), the characteristic values of W to be denoted ω (e.g., the mean value of a typical state variable of the system at the critical point) and the characteristic length $(D\theta)^{1/2}$. Denoting

$$\tilde{W} = W/\omega , \quad \tilde{t}=t/\theta , \quad \tilde{r}=\vec{\mathbf{r}}/(D\theta)^{1/2} , \quad \tilde{\nabla}=(D\theta)^{1/2}\vec{\nabla} ,$$
$$\tilde{f}(\tilde{r},\tilde{t}) = (\theta/\omega)[\theta(D\theta)^{d/2}]^{-1/2} f(\tilde{r},\tilde{t}) . \tag{B9}$$

Equation (B8) leads to

$$\frac{\partial}{\partial \tilde{t}}\tilde{W} = \tilde{\nabla}^2\tilde{W} + \lambda\tilde{W} + \tfrac{1}{2}\tilde{\nu}\tilde{W}^3 + \tilde{f}(\tilde{r},\tilde{t}) , \tag{B10}$$

where

$$\tilde{\lambda} = \theta\lambda , \tag{B11}$$

$$\tilde{\nu} = \tfrac{1}{2}\theta\omega^2\nu , \tag{B12}$$

and where

$$\langle \tilde{f}(\tilde{r},t)\tilde{f}(\tilde{r}',\tilde{t}')\rangle = \tilde{\Phi}\,\delta(\tilde{r}-\tilde{r}')\,\delta(\tilde{t}-\tilde{t}') , \tag{B13}$$

with

$$\tilde{\Phi} = [\theta/\omega^2(D\theta)^{d/2}]\Phi . \tag{B14}$$

In terms of the dimensionless quantities $\tilde{\Phi}$, $\tilde{\nu}$, and $\tilde{\lambda}$, the Ginzburg criterion (B6) takes the form

$$[4\tilde{\Phi}K_d\tilde{\nu}N/(2\pi)^d](1/2\lambda)^{(4-d)/2} \lesssim 1 , \tag{B15}$$

and assuming

$$4\tilde{K}_d\tilde{\nu}N/(2\pi)^d 2^{(4-d)} \sim O(1) , \tag{B16}$$

(B15) yields

$$\tilde{\Phi} \lesssim \tilde{\lambda}^{(4-d)/2} . \tag{B17}$$

Consider now the scaling procedure carried out on (B10). We put

$$\tilde{\lambda} = L^{-2}\tilde{\lambda}' , \quad \tilde{t}=L^2\tilde{t}' , \quad \tilde{W}=L^{-1}\tilde{W}' ,$$
$$\tilde{r}=L\tilde{r}' , \quad \tilde{\nu}=\tilde{\nu}' , \quad \tilde{\Phi}=\tilde{\Phi}' , \tag{B18}$$

to get

$$\frac{\partial}{\partial \tilde{t}'}\tilde{W}' = \tilde{\nabla}'^2\tilde{W}' + \tilde{\lambda}'\tilde{W}' + \tfrac{1}{2}\tilde{\nu}'\tilde{W}'^3 + L^{(4-d)/2}\tilde{f}(\tilde{r}',\tilde{t}') . \tag{B19}$$

A condition for the validity of this description is that the fluctuating term will remain lower or at most equal in order to the other terms in (B19), (these terms are all or order 1 after the scaling). This requires that

$$\tilde{\Phi} \lesssim L^{d-4} . \tag{B20}$$

In this relation the scaling parameter L is a measure of the distance from the critical point through the relation $\tilde{\lambda}' = L^2\tilde{\lambda} = O(1)$. Putting $L \simeq \tilde{\lambda}^{-1/2}$, we obtain again the inequality (B17). The condition for the validity of the scaling procedure in the presence of random fluctuations is thus seen to be equivalent to the Ginzburg condition for the validity of mean-field theory. In turn this observation makes it possible to derive similar conditions for cases involving generalized Langevin equations more complicated than (B1).

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which came from the dimensionality of the variables M are disregarded. Obviously all terms in the equations of motion have the same dimensionality and such contributions to scaling will cancel out.

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[15]It is convenient to make this transition to dimensionless quantities because we expect a need to compare the noise terms to the other terms in the deterministic equations. Having all quantities expressed in terms of their typical values, and having critical quantities scaled as done in Secs. III and IV we can generally assume that all the deterministic terms in the scaled equations are of order unity.

[16]In the Bernard instability studied in Ref. 6 only the fundamental mode in the vertical direction is considered. This leads to the vanishing of the nonlinear transport terms by symmetry requirements similar to those prevailing in the one-dimensional case studied in Appendix A.

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