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Stochastic Analysis of Symmetry-Breaking Bifurcations: Master Equation Approach

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The multivariate master equation for a general reaction-diffusion system is solved perturbatively, in the vicinity of a bifurcation point leading to symmetry-breaking transitions. The possibility to express the result through a Brazovskii type of potential is examined, and a comparison with the Langevin analysis of Walgraef *et al.* [*Adv. Chem. Phys.* **49**:311 (1982)] is performed.

KEY WORDS: Multivariate master equation; fluctuations; symmetry breaking; bifurcations.

1. INTRODUCTION

The stochastic description of nonlinear nonequilibrium systems in the vicinity of bifurcation points of new branches of solutions has been investigated extensively in the last years.$^{(1,2)}$ For reaction-diffusion systems, the transition from one homogeneous steady state to a bistable situation arising through a cusp bifurcation has been completely elucidated, using both master equation$^{(3)}$ and Langevin equation$^{(4)}$ approaches, combined with renormalization group techniques. In particular, it has been shown that the stationary distribution of inhomogeneous fluctuations is given by the exponential of a Landau–Ginzburg type of functional familiar from equilibrium phase transitions.

The problem of symmetry-breaking bifurcations beyond mean-field theory is considerably more involved. Important progress has been achieved by Swift and Hohenberg$^{(5)}$ for the Bénard instability and by Walgraef *et al.*$^{(6)}$ for chemical instabilities in infinitely extended systems,

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using a Langevin equation approach. Specifically, Walgraef *et al.* show that in bifurcations leading to steady state patterns, the stationary probability distribution is determined by a functional known as the Brazovskii potential.(7) This latter quantity differs from the Landau–Ginzburg functional in that it displays an additional quadratic term associated to the deviation of the wavelength from its critical value at the bifurcation point.

In infinite extended reaction-diffusion systems of two or more space dimensions, traditional bifurcation analysis reveals the possibility of transcritical branches associated with hysteresis and coexistence of a stable uniform state and a stable spatial pattern (Fig. 1a). In the probabilistic analysis(6) this shows up as the analog of a first-order transition. Contrary to its second-order counterpart, which occurs in a small vicinity of the bifur-

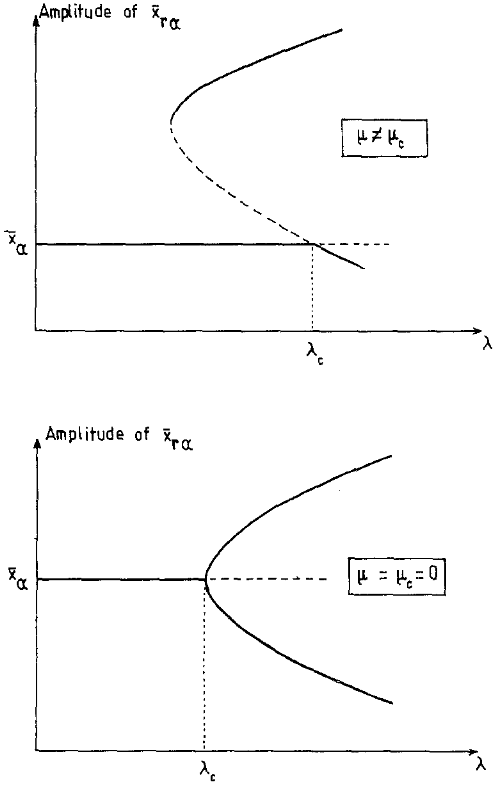

Fig. 1. (a) Bifurcation diagram exhibiting supercritical ($\lambda > \lambda_c$) as well as subcritical ($\lambda < \lambda_c$) branches. Full and dotted lines denote, respectively, stable and unstable solutions. The coalescence of the two subcritical branches takes place at a limit point which is generally distinct from λ_c as long as the other control parameters are different from critical values μ_c. (b) Degenerate situation (coalescence of bifurcation point and limit point) arising when $\mu = \mu_c$.

cation point, such a first-order transition is generally a global phenomenon, as the distance between the two simultaneously stable branches is not controlled by the bifurcation parameter.

Our aim in the present paper is twofold. First, we would like to investigate the status of the Brazovskii potential from the standpoint of the master equation approach. As is well known, in this approach, one incorporates at the starting point a great deal of physical information, such as the fact that chemical reactions define a birth and death process and that diffusion defines a random walk. Subsequently one tries to see whether, in some asymptotic sense, part of this information becomes "irrelevant" and one is reduced to a familiar problem of critical phenomena belonging to one or the other "universality class."

Our second objective relates to the global character of a first-order transition. When the phenomenon is controlled entirely by the bifurcation parameter λ (like in a second-order transition) one can set up a perturbative expansion of the master equation,(3) and determine the conditions under which the initial stochastic process is reduced to a diffusion process amenable to a Langevin equation subjected to additive Gaussian white noise. But when the distance between states is finite the above perturbation method is no longer legitimate. One can of course always extrapolate it on the basis of phenomenological arguments, but it is quite possible that in this way consistency is not guaranteed. We believe that the way out of this difficulty is to transform the global problem to a local one, by displaying a second control parameter μ built into the system. This parameter should vary in such a way that when $\lambda \to \lambda_c$, μ should tend to a value μ_c (hereafter taken to be zero), such that the limit point tends to the bifurcation point (Fig. 1b). Such a problem would thus remain tractable within the realm of a perturbative approach.

In Section 2 we write the multivariate master equation for a general reaction-diffusion system and seek solutions displaying the exponential of a stochastic potential U. This leads us, to the dominant order in the size of the system, to a multivariate Hamilton–Jacobi equation.(8,9) From this we deduce a set of equations for the successive derivatives (up to the fourth) of the stochastic potential with respect to the state variables.

In Section 3 we express the stochastic potential in the representation provided by the eigenfunctions of an operator related to the linearized operator of the phenomenological mass balance equations and estimate the orders of magnitude of the different terms present. Section 4 is devoted to the solution of the equations of the successive derivatives of U in this representation and to the comparison of the result to the Brazovskii potential. In Section 5 we illustrate the general expressions on the Brusselator model,(1) and compare with the work by Walgraef *et al.*(6) In the final section we discuss the interest of the method and suggest some problems for future investigations.

Throughout the paper we insist on the general procedure and on the qualitative aspects of the problem. (Technical details are to be found in Ref. 11.)

2. THE MULTIVARIATE HAMILTON–JACOBI EQUATION FOR A REACTION–DIFFUSION SYSTEM

Let $\{X_\alpha\}$ be a set of ϕ chemically active constituents in a volume V in a d-dimensional space. This space is divided into n submacroscopic cells. The numbers of cells along each axis are denoted by $n_1, n_2, \ldots, n_d$ such that $n_1 \times n_2 \times \cdots \times n_d = n$. A vector $\mathbf{r} = (r_1, r_2, \ldots, r_d)$ with integer components locates a given cell.

The number of particles of species α in cell $\mathbf{r}$ will be denoted $X_{\mathbf{r}\alpha}$. The kinetic characteristics of the chemical reactions are the following:

$\bar{\nu}_{\rho\alpha}$, order of the ρth reaction with respect to X_α;
$\nu_{\rho\alpha}$, stoichiometric coefficient of X_α in the ρth reaction ($\nu_{\rho\alpha} > 0$ for particles formed as a result of the reaction and $\nu_{\rho\alpha} < 0$ for particles disappearing as a result of the reaction);
k_ρ, kinetic constant of the ρth reaction expressed in $(\text{second})^{-1} \cdot (\text{liter})^{\Sigma_\alpha \bar{\nu}_{\rho\alpha} - 1}$ units.

These constants may include externally controlled concentrations.

Each constituent X_α may diffuse between two adjacent cells with a jump frequency D_α depending on the size of the cell and related to Fick's coefficient $\mathscr{D}_\alpha$ through

$$\frac{D_\alpha}{2d} (\Delta l)^2 \sim \mathscr{D}_\alpha$$

where Δl is the length of the cell.

The usual$^{(1,3,9)}$ stochastic description of the chemical reaction as birth and death processes and of diffusion as random walk between adjacent cells, leads to the multivariate master equation:

$$\begin{aligned}\frac{dP}{dt} &= \sum_\rho k_\rho (\Delta V)^{1 - \Sigma_\alpha \bar{\nu}_{\rho\alpha}} \\ &\quad \times \sum_{\mathbf{r}} \left\{ \left[\prod_\alpha \frac{(X_{\mathbf{r}\alpha} - \nu_{\rho\alpha})!}{(X_{\mathbf{r}\alpha} - \bar{\nu}_{\rho\alpha} - \nu_{\rho\alpha})!} \right] P(\{X_{\mathbf{r}\alpha} - \nu_{\rho\alpha}\}) - \left[\prod_\alpha \frac{X_{\mathbf{r}\alpha}!}{(X_{\mathbf{r}\alpha} - \bar{\nu}_{\rho\alpha})!} \right] P \right\} \\ &\quad + \sum_\alpha \frac{D_\alpha}{2d} \sum_{\mathbf{r}\mathbf{a}} [(X_{\mathbf{r}\alpha} + 1) P(X_{\mathbf{r}\alpha} + 1, X_{(\mathbf{r}+\mathbf{a})\alpha} - 1) - X_{\mathbf{r}\alpha} P] \qquad (1)\end{aligned}$$

ΔV is the volume of one cell, and $\mathbf{a}$ denotes the first neighbors of cell $\mathbf{r}$. P is a function of the set of variables $\{X_{\mathbf{r}\alpha}\}$. Only the values of the arguments of P which differ from $\{X_{\mathbf{r}\alpha}\}$ are explicitly indicated.

Denoting by N_t the mean total number of particles in the system and $N = N_t/n$ the mean number of particles in one cell, we set$^{(8,9)}$

$$x_{\mathbf{r}\alpha} = \frac{X_{\mathbf{r}\alpha}}{N}$$

and

$$P(\{X_{\mathbf{r}\alpha}\}, t) = p(\{x_{\mathbf{r}\alpha}\}, t) = e^{-S-NU(\{x_{\mathbf{r}\alpha}\}, t)} \tag{2}$$

where the stochastic potential $U(\{x_{\mathbf{r}\alpha}\}, t)$ is considered as a function of continuous variables and S is introduced to normalize p.

Dividing the two sides of Eq. (1) by NP, expanding the right-hand side in terms of $1/N$, and setting

$$\bar{k}_\rho = k_\rho \left(\frac{\Delta V}{N}\right)^{1-\Sigma_\alpha \bar{\nu}_{\rho\alpha}}$$

we obtain, to zeroth order in $1/N$, a Hamilton–Jacobi type of equation$^{(8,9)}$:

$$\begin{aligned} -\frac{1}{N}\frac{dS}{dt} - \frac{\partial U}{\partial t} = {} & \sum_\rho \bar{k}_\rho \sum_{\mathbf{r}} \left(\prod_\alpha x_{\mathbf{r}\alpha}^{\bar{\nu}_{\rho\alpha}}\right)\left[\exp\left(\sum_\alpha \nu_{\rho\alpha}\frac{\partial U}{\partial x_{\mathbf{r}\alpha}}\right) - 1\right] \\ & + \frac{1}{2d}\sum_\alpha D_\alpha \sum_{\mathbf{ra}} x_{\mathbf{r}\alpha}\left[\exp\left(-\frac{\partial U}{\partial x_{\mathbf{r}\alpha}} + \frac{\partial U}{\partial x_{(\mathbf{r}+\mathbf{a})\alpha}}\right) - 1\right] \end{aligned} \tag{3}$$

This equation may also be written in the following form, which defines the "Hamiltonian" H:

$$\frac{1}{N}\frac{dS}{dt} + \frac{\partial U}{\partial t} + H\left(\{x_{\mathbf{r}\alpha}\}, \left\{\frac{\partial U}{\partial x_{\mathbf{r}\alpha}}\right\}\right) = 0 \tag{4}$$

We are interested primarily in situations in which a certain reference state $\{\bar{x}_\alpha\}$, corresponding to a uniform steady state solution of the phenomenological reaction-diffusion equations, loses its stability and gives rise to nonuniform states $\{\bar{x}_{\mathbf{r}\alpha}\}$. We expect that in the vicinity of the transition the distribution around $\{\bar{x}_{\mathbf{r}\alpha}\}$ will no longer be Gaussian.$^{(1-4,9)}$ It follows that an expansion of U around $\{\bar{x}_{\mathbf{r}\alpha}\}$, truncated to second-order terms,$^{(10)}$ is not sufficient. Postponing until Section 3 the question of consistency we here attempt to determine the terms needed in an expansion of U up to fourth order:

$$U(\{x_{\mathbf{r}\alpha}\}) = U(\{\bar{x}_{\mathbf{r}\alpha}\}) + \frac{1}{2} \sum_{\mathbf{r}_1\alpha_1\mathbf{r}_2\alpha_2} \frac{\partial^2 U}{\partial x_{\mathbf{r}_1\alpha_1}\,\partial x_{\mathbf{r}_2\alpha_2}} \xi_{\mathbf{r}_1\alpha_1}\xi_{\mathbf{r}_2\alpha_2}$$
$$+ \frac{1}{6} \sum_{\mathbf{r}_1\alpha_1\mathbf{r}_2\alpha_2\mathbf{r}_3\alpha_3} \frac{\partial^3 U}{\partial x_{\mathbf{r}_1\alpha_1}\,\partial x_{\mathbf{r}_2\alpha_2}\,\partial x_{\mathbf{r}_3\alpha_3}} \xi_{\mathbf{r}_1\alpha_1}\xi_{\mathbf{r}_2\alpha_2}\xi_{\mathbf{r}_3\alpha_3}$$
$$+ \frac{1}{24} \sum_{\mathbf{r}_1\alpha_1\mathbf{r}_2\alpha_2\mathbf{r}_3\alpha_3\mathbf{r}_4\alpha_4} \frac{\partial^4 U}{\partial x_{\mathbf{r}_1\alpha_1}\,\partial x_{\mathbf{r}_2\alpha_2}\,\partial x_{\mathbf{r}_3\alpha_3}\,\partial x_{\mathbf{r}_4\alpha_4}}$$
$$\times\, \xi_{\mathbf{r}_1\alpha_1}\xi_{\mathbf{r}_2\alpha_2}\xi_{\mathbf{r}_3\alpha_3}\xi_{\mathbf{r}_4\alpha_4} \tag{5a}$$

with

$$\xi_{\mathbf{r}\alpha} = x_{\mathbf{r}\alpha} - \bar{x}_{\mathbf{r}\alpha} \tag{5b}$$

Note the absence of first-order terms, owing to the fact that U is extremum on the solutions of phenomenological rate equations. In the sequel we also discard the constant term $U(\{\bar{x}_{\mathbf{r}\alpha}\})$, which can always be incorporated in the normalization constant. To facilitate the calculations we also introduce the shorthand notations

$$x_{\mathbf{r}\alpha} = x_i$$
$$\left(\frac{\partial^2 U}{\partial x_i\,\partial x_j}\right)_{\bar{x}} = U^{ij} \tag{5c}$$
$$\text{etc.}$$

The problem now amounts to finding the equations from which successive derivatives U^{ij}, U^{ijk}, U^{ijkl} can be determined. To this end one has to expand both sides of Eq. (4) in powers of $\xi_i = x_i - \bar{x}_i$ and identify coefficients up to fourth order. On inspecting the explicit structure of the function H [cf. Eqs. (3) and (4)] we see that various powers of ξ_i are obtained by differentiating successively H either with respect of $\{x_j\}$ or with respect of $\{\partial U/\partial x_j\}$, and evaluating the result at the deterministic values $\{\bar{x}_j\}$. We therefore introduce the notations

$$\frac{\partial H}{\partial(\partial U/\partial x_i)} = H_i, \qquad \frac{\partial^2 H}{\partial(\partial U/\partial x_i)\,\partial(\partial U/\partial x_j)} = H_{ij}, \qquad \text{etc.} \tag{6a}$$

$$\frac{\partial^2 H}{\partial x_i\,\partial(\partial U/\partial x_j)} = H^i_j, \qquad \frac{\partial^3 H}{\partial x_i\,\partial x_j\,\partial(\partial U/\partial x_k)} = H^{ij}_k, \qquad \text{etc.} \tag{6b}$$

Using the explicit form of H one can show the following:

(i) H^j_i evaluated at $\{\bar{x}_i\}$ is identical to the linearized operator $\mathscr{L}$ associated to the deterministic rate equations.

(ii) H_i, H_{ij}, etc. are identical to the expressions of the first, second, etc. moments of the transition probability [cf. Eq. (1)] except for the combinatorial factor.

(iii) $H^j_{i_1 \cdots i_n}$ is the first derivative of the nth transition moment (without combinatorial factor) with respect to x_j. Similarly $H^{j_1 j_2}_{i_1 \cdots i_n}$ is a second derivative, and so forth.

In what follows, it is understood that all these expressions are to be evaluated at the deterministic state $\{\bar{x}_i\}$.

Two quantities for which we need more explicit expressions in Sections 4 and 5 are H^{ij}_k and H^{ijk}_l, evaluated at a uniform reference state $\{\bar{x}_\alpha\}$.

Using Eq. (6) and the definition of H, we have

$$H^{\mathbf{r}\alpha\,\mathbf{r}'\alpha'}_{\mathbf{r}''\alpha''} = \delta(\mathbf{r}-\mathbf{r}')\,\delta(\mathbf{r}-\mathbf{r}'')\,M^{\alpha\alpha'}_{\alpha''} \tag{7a}$$

$$H^{\mathbf{r}\alpha\,\mathbf{r}'\alpha'\mathbf{r}''\alpha''}_{\mathbf{r}'''\alpha'''} = \delta(\mathbf{r}-\mathbf{r}')\,\delta(\mathbf{r}-\mathbf{r}'')\,\delta(\mathbf{r}-\mathbf{r}''')\,M^{\alpha\alpha'\alpha''}_{\alpha'''} \tag{7b}$$

where $M^{\alpha\alpha'}_{\alpha''}$, $M^{\alpha\alpha'\alpha''}_{\alpha'''}$ are the second and third derivatives of the first chemical transition moment:

$$M_\alpha = \sum_\rho \bar{k}_\rho \nu_{\rho\alpha} \prod_\beta \bar{x}_\beta^{\bar{\nu}_{\rho\beta}} \tag{7c}$$

We are now in a position to write the equations obtained in various orders in $\{\xi_i\}$. To zeroth order one merely obtains the discretized form of the phenomenological reaction-diffusion equations:

$$\begin{aligned}\frac{d\bar{x}_{\mathbf{r}\alpha}}{dt} &= \sum_\rho \bar{k}_\rho \nu_{\rho\alpha} \prod_\beta \bar{x}_{\mathbf{r}\beta}^{\bar{\nu}_{\rho\beta}} + \frac{D_\alpha}{2d} \sum_{\mathbf{a}} (\bar{x}_{(\mathbf{r}+\mathbf{a})\alpha} - \bar{x}_{\mathbf{r}\alpha}) \\ &\equiv M_{\mathbf{r}\alpha}(\{\bar{x}_{\mathbf{r}\beta}\}, \lambda, \mu, \ldots) + \frac{D_\alpha}{2d} \sum_{\mathbf{r}'\mathbf{a}} [\delta(\mathbf{r}+\mathbf{a}-\mathbf{r}') - \delta(\mathbf{r}-\mathbf{r}')]\,\bar{x}_{\mathbf{r}'\alpha}\end{aligned} \tag{8}$$

in which the first chemical transition moment in cell $\mathbf{r}$, $M_{\mathbf{r}\alpha}$ denotes the net effect of reactions and $\lambda, \mu, \ldots$ stand for the parameters controlling the various transition phenomena.

To higher orders in $\{\xi_i\}$ one obtains the equations for successive derivatives of the potential U. Adopting the convention that repeated indices are summed over, we obtain

$$-\frac{d}{dt} U^{ij} = \mathscr{S}_{ij}\{U^{ih} H^j_h\} + U^{ih_1} U^{jh_2} H_{h_1 h_2} \tag{9a}$$

$$\begin{aligned}-\frac{d}{dt} U^{ijk} = \mathscr{S}_{ijk}\{&U^{ijh_1}(H^k_{h_1} + U^{kh_2} H_{h_1 h_2}) + U^{ih} H^{jk}_h + U^{ih_1} U^{jh_2} H^k_{h_1 h_2}\} \\ &+ U^{ih_1} U^{jh_2} U^{kh_3} H_{h_1 h_2 h_3}\end{aligned} \tag{9b}$$

$$
\begin{aligned}
-\frac{d}{dt}U^{ijkl} = \mathscr{S}_{ijkl}\{&U^{ijkh_1}(H^{l}_{h_1} + U^{lh_2}H_{h_1h_2}) + U^{ijh}H^{kl}_{h} + U^{ijh_1}U^{kh_2}H^{l}_{h_1h_2} \\
&+ U^{ijh_1}U^{kh_2}U^{lh_3}H_{h_1h_2h_3} + U^{ijh_1}U^{klh_2}H_{h_1h_2} \\
&+ U^{ih}H^{jkl}_{h} + U^{ih_1}U^{jh_2}H^{kl}_{h_1h_2} + U^{ih_1}U^{jh_2}U^{kh_3}H^{l}_{h_1h_2h_3}\} \\
&+ U^{ih_1}U^{jh_2}U^{kh_3}U^{lh_4}H_{h_1h_2h_3h_4}
\end{aligned}
\tag{9c}
$$

The symmetrization symbol $\mathscr{S}_{ij\ldots}$, applied to a function of the indices $i, j, \ldots$, represents the sum of all distinct terms obtained by permutation of these indices.

3. STOCHASTIC POTENTIAL IN THE VICINITY OF A TRANSITION

For a general reaction-diffusion system, Eqs. (9a)–(9c) constitute a complex set of relations. In this section we explore some of the simplifications that arise when the system operates in the vicinity of the transition point. By definition, in this case the linearized operator $\mathscr{L}$ has one eigenvalue that goes to zero or a pair of purely imaginary eigenvalues. Hereafter we are interested exclusively in real eigenvalues, which characterize the bifurcation of time-independent (and possibly space-dependent) solutions.

As pointed out in the previous section, the operator H^{j}_{i} evaluated at the reference state $\{\bar{x}_i\}$ is identical to the linearized stability operator. Utilizing the explicit form, Eq. (8), of the reaction-diffusion equations, we can write

$$
H^{\mathbf{r}'\alpha'}_{\mathbf{r}\alpha} = \mathscr{L}^{\mathbf{r}'\alpha'}_{\mathbf{r}\alpha} = \left(\frac{\partial M_{\mathbf{r}\alpha}}{\partial x_{\mathbf{r}'\alpha'}}\right)_{\{\bar{x}_\alpha\}} + \frac{D_\alpha}{2d}\,\delta_{\alpha\alpha'}\sum_{\mathbf{a}}\,[\delta(\mathbf{r}+\mathbf{a}-\mathbf{r}') - \delta(\mathbf{r}-\mathbf{r}')]
\tag{10}
$$

From now on, the reference state is chosen to be the uniform steady state $\{\bar{x}_\alpha\}$. As a result, $(\partial M_{\mathbf{r}\alpha}/\partial x_{\mathbf{r}'\alpha'})_{\{\bar{x}_\alpha\}}$ becomes independent of $\mathbf{r}$ and $\mathbf{r}'$ and will be noted $M^{\alpha'}_{\alpha}\,\delta(\mathbf{r}-\mathbf{r}')$.

Because of the presence of a space-dependent part, in a system of large spatial extension the transition to instability will be marked not only by one well-separated eigenvalue going to zero but rather by the accumulation to zero of a large number of closely packed eigenvalues.

For periodic boundary conditions, suitable for describing systems of large size, the eigenvectors $\mathbf{C}^{\mathbf{m}\alpha}$ of (10) have the following components:

$$
C^{\mathbf{m}\alpha}_{\mathbf{r}\alpha'} = \frac{1}{\sqrt{n}}\,(c_{\mathbf{m}})^{\alpha}_{\alpha'}\,e^{i\,\mathbf{r}\cdot\mathbf{m}}
\tag{11}
$$

Note that $\mathbf{m}$ plays the role of a Fourier variable, whereas α refers to the space of chemical concentrations. As usual in Fourier expansions, a normalizing factor $1/\sqrt{n}$ has been introduced. Thanks to (11), the eigenvalues $\omega_{\mathbf{m}\alpha}$ can be evaluated from

$$\sum_{\beta} \left[M_{\alpha}^{\beta} - \sum_{\mathbf{a}} (1 - e^{-i\mathbf{m}\cdot\mathbf{a}}) \frac{D_{\alpha}}{2d} \delta_{\alpha\beta} \right] (c_{\mathbf{m}})_{\beta}^{\alpha'} = \omega_{\mathbf{m}\alpha'} (c_{\mathbf{m}})_{\alpha}^{\alpha'} \tag{12}$$

In symmetry-breaking instabilities, the vanishing of one of the eigenvalues $\omega_{\mathbf{m}\alpha}$ at a transition point will imply conditions on $\mathbf{m}$. We denote by $\mathbf{m}_c$ this critical set. In an infinitely extended system, the critical set is simply the sphere $|\mathbf{m}| = m_c = \text{given number}$. For $\mathbf{m} = \mathbf{m}_c$, only one eigenvalue vanishes at the transition point, which will be denoted by $\omega_{\mathbf{m}_c \alpha_c}$.

Let us now see the repercussions of the above properties on the solutions of Eqs. (9). All of these equations except Eq. (9a) for U^{ij} are linear and can be solved once U^{ij} is known. The central quantity to determine is therefore U^{ij}. To evaluate it, we place ourselves on the reference state in which case $dU^{ij}/dt = 0$. Introducing the inverse matrix U_{ij}^{-1}, we can then write Eq. (9a) as

$$\mathscr{S}_{ij}\{H_i^h U_{hj}^{-1}\} = -H_{ij} \tag{13}$$

In the representation which diagonalizes the linear stability operator $\mathscr{L}$ ($\mathscr{L}_i^j = H_i^j$), we can further simplify (13) to

$$(\omega_i + \omega_j)\, {}^{C}U_{ij}^{-1} = -{}^{C}H_{ij} \tag{14}$$

where ${}^{C}\mathsf{U}^{-1}$, ${}^{C}\mathsf{H}$ are the transforms of U^{-1}, H in the eigenspace of $\mathscr{L}$. Note that the index i is now an abbreviation for $(\mathbf{m}\alpha)$ rather than $(\mathbf{r}\alpha)$ as before.

We see clearly that in a transition point, $\omega_i = 0$, U is not invertible. On the other hand, Eq. (14) allows us to relate its eigenvectors $\mathbf{Q}^i$ and eigenvalues ε_i to those of $\mathscr{L}$. In fact, in most cases we will only need to establish this connection for values of i such that ω_i is close to the critical eigenvalue $\omega_{i_c} = 0$. Denoting by i_0 this set, we obtain, to dominate order, after some algebra

$$\begin{gathered} \varepsilon_{i_0} \simeq -2\frac{\omega_{i_0}}{l_c} \\ \mathbf{Q}^{i_0} \simeq \mathbf{C}^{i_0} \end{gathered} \tag{15a}$$

in which l_c is a constant defined by

$${}^{C}H_{\mathbf{m}_c\alpha_c\mathbf{m}'_c\alpha_c} = \delta(\mathbf{m}_c + \mathbf{m}'_c)\ l_c \tag{15b}$$

and whose value is model dependent.

In view of the intimate connection between U^{ij} and $\mathscr{L}$, it is now natural to express the stochastic potential Eq. (5a) in a representation diagonalizing U^{ij}. Defining the transformed variables

$$\zeta_i = \frac{1}{\sqrt{n}} Q^{-1}{}_i^h \xi_h \tag{16}$$

we obtain

$$U = n\left(\frac{1}{2}\sum_i \varepsilon_i \zeta_i \zeta_i^* + \frac{1}{6}\sum_{ijk} \bar{U}^{ijk}\zeta_i\zeta_j\zeta_k + \frac{1}{24}\sum_{ijkl} \bar{U}^{ijkl}\zeta_i\zeta_j\zeta_k\zeta_l + \cdots\right) \tag{17}$$

where $\bar{U}^{ijk} = \sqrt{n}\ {}^{Q}U^{ijk}$, $\bar{U}^{ijkl} = n\ {}^{Q}U^{ijkl}$, ${}^{Q}U^{ijk}$, ${}^{Q}U^{ijkl}$ being the transforms of U^{ijk}, U^{ijkl} in the new representation.

By its definition, Eq. (2), U must be proportional to the total number of cells n. This is achieved in Eq. (17) through the factor n multiplying the square bracket.

Let us now come to the orders of magnitude in terms of the system's parameters, particularly those controlling the distance from the bifurcation point and the limit point (cf. Fig. 1). We first recall that if all ε_i's are finite and positive, there is no need to go further than the quadratic terms in Eq. (17), and the amplitude of ζ can be limited to the order of $1/\sqrt{n}$ for the corresponding states to have a nonnegligible probability. But when one of ε_i's becomes small, $\varepsilon_i = \varepsilon_{i_0}$, the corresponding critical mode ζ_{i_0} cannot be described adequately unless higher-order terms are included. Comparing first quadratic and quartic terms we see that for finite $\bar{U}^{ijkl}$, they are comparable if $|\varepsilon_{i_0}| \sim |\zeta|^2$, which defines a small neighborhood of the bifurcation point $\varepsilon_{i_c} = 0$ or $\lambda = \lambda_c$. Coming next to the cubic terms, knowing from the above argument that $|\zeta_{i_0}| \sim |\varepsilon_{i_0}|^{1/2}$, we see that one way that these terms can be comparable to the quadratic and quartic ones is

$$|\bar{U}^{i_0 j_0 k_0}| \sim |\varepsilon_{i_0}|^{1/2} \tag{18a}$$

Inasmuch as $|\varepsilon_{i_0}|^{1/2}$ itself is of the order of $(\lambda - \lambda_c)^b$, b being in general smaller than or equal to 1, we conclude that there must be a second parameter μ, in the problem, controlling the magnitude of $\bar{U}^{i_0 j_0 k_0}$ through

$$\begin{aligned} |\bar{U}^{i_0 j_0 k_0}| &\sim O(\mu) \\ \mu &\sim (\lambda - \lambda_c)^b \end{aligned} \tag{18b}$$

The only other way cubic terms can influence the stochastic potential is through the presence of one noncritical mode:

$$\bar{U}^{i_0 j_0 k_0}\zeta_{i_0}\zeta_{j_0}\zeta_k \tag{18c}$$

provided that $\bar{U}^{i_0 j_0 k}$ is of $O(1)$ and ζ_k of $O(|\varepsilon_{k_0}|)$ for $k \neq k_0$.

Summarizing, we can write the following stochastic potential which is consistent with all requirements of perturbation theory:

$$
\begin{aligned}
U = n \Bigg[& \frac{1}{2} \sum_{i} \varepsilon_i \zeta_i \zeta_i^* + \frac{1}{6} \Bigg(\sum_{i_0 j_0 k_0} \bar{U}^{i_0 j_0 k_0} \zeta_{i_0} \zeta_{j_0} \zeta_{k_0} \\
& + 3 \sum_{i_0 j_0 k \neq k_0} \bar{U}^{i_0 j_0 k} \zeta_{i_0} \zeta_{j_0} \zeta_k \Bigg) \\
& + \frac{1}{24} \sum_{i_0 j_0 k_0 l_0} \bar{U}^{i_0 j_0 k_0 l_0} \zeta_{i_0} \zeta_{j_0} \zeta_{k_0} \zeta_{l_0} \Bigg]
\end{aligned}
\tag{19a}
$$

Before we proceed to the evaluation of the different coefficients appearing in Eq. (19a) it will be useful to write the potential in a form exhibiting separately the contributions from the critical modes and those containing at least one non-critical mode:

$$
\begin{aligned}
U = n \Bigg(& \frac{1}{2} \sum_{i_0} \varepsilon_{i_0} \zeta_{i_0} \zeta_{i_0}^* + \frac{1}{6} \sum_{i_0 j_0 k_0} \bar{U}^{i_0 j_0 k_0} \zeta_{i_0} \zeta_{j_0} \zeta_{k_0} \\
& + \frac{1}{24} \sum_{i_0 j_0 k_0 l_0} \bar{U}^{i_0 j_0 k_0 l_0} \zeta_{i_0} \zeta_{j_0} \zeta_{k_0} \zeta_{l_0} \Bigg) \\
& + n \frac{1}{2} \Bigg(\sum_{i \neq i_0} \varepsilon_i \zeta_i \zeta_i^* + \sum_{(i \neq i_0), j_0 k_0} \bar{U}^{i j_0 k_0} \zeta_i \zeta_{j_0} \zeta_{k_0} \Bigg)
\end{aligned}
\tag{19b}
$$

By slightly transforming the second bracket we further obtain

$$
\begin{aligned}
U = n \Bigg[& \frac{1}{2} \sum_{i_0} \varepsilon_{i_0} \zeta_{i_0} \zeta_{i_0}^* + \frac{1}{6} \sum_{i_0 j_0 k_0} \bar{U}^{i_0 j_0 k_0} \zeta_{i_0} \zeta_{j_0} \zeta_{k_0} \\
& + \frac{1}{24} \sum_{i_0 j_0 k_0 l_0} \left(\bar{U}^{i_0 j_0 k_0 l_0} - 3 \sum_{h \neq h_0} \bar{U}^{i_0 j_0 h} \frac{1}{\varepsilon_h} \bar{U}^{h k_0 l_0} \right) \zeta_{i_0} \zeta_{j_0} \zeta_{k_0} \zeta_{l_0} \Bigg] \\
& + \frac{n}{2} \sum_{i \neq i_0} \varepsilon_i \left(\zeta_i + \frac{1}{2\varepsilon_i} \sum_{k_0 l_0} \bar{U}^{i k_0 l_0} \zeta_{k_0} \zeta_{l_0} \right) \left(\zeta_i + \frac{1}{2\varepsilon_i} \sum_{k_0' l_0'} \bar{U}^{i k_0' l_0'} \zeta_{k_0'} \zeta_{l_0'} \right)^*
\end{aligned}
\tag{19c}
$$

The probability associated to this potential is the product of a multivariate Gaussian distribution with respect to the noncritical modes, centered in

$$
\zeta_i = \frac{-1}{2\varepsilon_i} \sum_{k_0 l_0} \bar{U}^{i k_0 l_0} \zeta_{k_0} \zeta_{l_0}
\tag{20}
$$

and of a distribution restricted to the critical modes only: $P \propto e^{-NU_{\mathrm{cr}}}$ with

$$U_{\mathrm{cr}} = n \left[\frac{1}{2} \sum_{i_0} \varepsilon_{i_0} \zeta_{i_0} \zeta_{i_0}^* + \frac{1}{6} \sum_{i_0 j_0 k_0} \bar{U}^{i_0 j_0 k_0} \zeta_{i_0} \zeta_{j_0} \zeta_{k_0} \right.$$
$$\left. + \frac{1}{24} \sum_{i_0 j_0 k_0 l_0} \left(\bar{U}^{i_0 j_0 k_0 l_0} - 3 \sum_{h \neq h_0} \bar{U}^{i_0 j_0 h} \frac{1}{\varepsilon_h} \bar{U}^{h k_0 l_0} \right) \zeta_{i_0} \zeta_{j_0} \zeta_{k_0} \zeta_{l_0} \right] \qquad (21)$$

This provides the justification of the "adiabatic elimination" of the noncritical modes used in Ref. 6.

4. EVALUATION OF THE COEFFICIENTS OF CUBIC AND QUARTIC TERMS

Our next step is to evaluate the coefficients $\bar{U}^{i_0 j_0 k_0}$, $\bar{U}^{i_0 j_0 k}$ and $\bar{U}^{i_0 j_0 k_0 l_0}$, using Eqs. (9b) and (9c) in which U^{ij} is given by Eq. (14). As before, we will carry out this calculation using the homogeneous stationary solution as reference state. This will allow us to limit ourselves to the time-independent solutions of (9b) and (9c). To simplify as much as possible the rather heavy initial expressions, we shall take advantage of the parameter dependence of the various quantities, as discussed in the preceding section.

4.1. Cubic Terms

Utilizing Eq. (9a) at its steady state and switching as before to the representation diagonalizing U^{ij} we obtain

$$\mathscr{S}_{ijk} \left\{ \varepsilon_i \frac{{}^Q H_{\bar{\imath}}^h}{\varepsilon_h} {}^Q U^{\bar{h} jk} \right\} = \mathscr{S}_{ijk} \{ \varepsilon_i \, {}^Q H_{\bar{\imath}}^{jk} + \varepsilon_i \varepsilon_j \, {}^Q H_{\bar{\imath}\bar{\jmath}}^{k} + \varepsilon_i \varepsilon_j \varepsilon_k \, {}^Q H_{\overline{\imath\jmath k}} \} \qquad (22a)$$

where the index $\bar{\imath}$ has the same α part as i but an opposite Fourier variable $\bar{\mathbf{m}} = -\mathbf{m}$ (mod 2π).

When all i, j are close to the critical set ($i = i_0$, $j = j_0$) the last two terms of this equation become negligible. Moreover, if $k \neq k_0$, only one of the terms coming from the symmetrization operator is nonnegligible. We thus obtain

$$\frac{{}^Q H_k^h}{\varepsilon_h} {}^Q U^{\bar{h} i_0 j_0} = {}^Q H_k^{i_0 j_0} \qquad (22b)$$

It can be verified that even if $k = k_0$, Eq. (22a) admits a solution of the form given by Eq. (22b). Because of the linearity in ${}^Q U^{hjk}$, this must be the only solution. From now on therefore we can extend Eq. (22b) to $k = k_0$ as well.

To solve for ${}^{Q}U^{i_0 j_0 k}$ one has to invert the operator $({}^{Q}H_{k}^{h}/\varepsilon_h)$. As ${}^{Q}H_{k}^{h}$ is related to H_{k}^{h} by a similarity transformation, it has the same eigenvalues ω_i as the linearized stability operator $\mathscr{L}$ ($\mathscr{L}_{i}^{j} = H_{i}^{j}$). It therefore becomes singular in the vicinity of bifurcation. In this case, however, ε_h vanishes as ω_h [cf. Eq. (15a)]. As a result, the operator $({}^{Q}H_{k}^{h}/\varepsilon_h)$ is always invertible. The solution of Eq. (22b) is thus

$$ {}^{Q}U^{i_0 j_0 k} = \varepsilon_k \frac{(\mathbf{Q}^{k} \cdot \mathbf{C}^{\bar{h}})}{\omega_h} \, {}^{C}H_{h}^{i_0 j_0} \tag{22c} $$

where ${}^{C}H_{h}^{i_0 j_0}$ is now expressed in the eigenspace of the linearized stability operator.

To obtain more explicit expressions, one has to invoke definitions (7) and subsequent remarks made in Section 2. This yields

$$ \begin{aligned} \bar{U}^{\mathbf{m}_0 \alpha_c \mathbf{m}_0' \alpha_c \mathbf{m}'' \alpha} &= \sqrt{n} \, {}^{Q}U^{\mathbf{m}_0 \alpha_c \mathbf{m}_0' \alpha_c \mathbf{m}'' \alpha} \\ &= \delta(\mathbf{m}_0 + \mathbf{m}_0' + \mathbf{m}'') \, \varepsilon_{\mathbf{m}'' \alpha} \frac{(\mathbf{q}_{\mathbf{m}''})^{\alpha} \cdot (\mathbf{c}_{\mathbf{m}''})^{\beta}}{\omega_{\mathbf{m}'' \beta}} \\ &\quad \times (c_{\mathbf{m}''}^{-1})_{\beta}^{\beta_1} M_{\beta_1}^{\beta_2 \beta_3} (c_{\mathbf{m}_0})_{\beta_2}^{\alpha_c} (c_{\mathbf{m}_0'})_{\beta_3}^{\alpha_c} \end{aligned} \tag{23a} $$

where $(\mathbf{c}_{\mathbf{m}})^{\beta}$ has been defined in Eq. (11) and $(\mathbf{q}_{\mathbf{m}})^{\alpha}$ is introduced in a similar way through the equation

$$ Q_{\mathbf{r}\alpha'}^{\mathbf{m}\alpha} = \frac{1}{\sqrt{n}} (q_{\mathbf{m}})_{\alpha'}^{\alpha} \, e^{i \mathbf{m} \cdot \mathbf{r}} \tag{23b} $$

An additional simplification is achieved when $\mathbf{m}'' = \mathbf{m}_0''$ and $\alpha = \alpha_c$. Using Eq. (15a) relating $\varepsilon_{\mathbf{m}_0 \alpha_c}$ and $\mathbf{Q}^{\mathbf{m}_0 \alpha_c}$ to the properties of the linearized stability operator we obtain

$$ \begin{aligned} \bar{U}^{\mathbf{m}_0 \alpha_c \mathbf{m}_0' \alpha_c \mathbf{m}_0'' \alpha_c} &= -\frac{2}{l_c} (c_{\mathbf{m}_0''}^{-1})_{\alpha_c}^{\beta_1} M_{\beta_1}^{\beta_2 \beta_3} (c_{\mathbf{m}_0})_{\beta_2}^{\alpha_c} (c_{\mathbf{m}_0'})_{\beta_3}^{\alpha_c} \\ &\quad \times \delta(\mathbf{m}_0 + \mathbf{m}_0' + \mathbf{m}_0'') \end{aligned} \tag{23c} $$

Note that when $\mathbf{m}'' = \mathbf{m}_0''$ and $\alpha \neq \alpha_c$, the divergent component obtained for $\beta = \alpha_c$ in the sum (23a), vanishes because of the orthogonality of $(\mathbf{q}_{\mathbf{m}_0''})^{\alpha}$ and $(\mathbf{c}_{\mathbf{m}_0''})^{\alpha_c}$ [cf. Eq. (15a)].

On the other hand, the factor multiplying the Kronecker delta in (23c), is a scalar since the eigenvectors $(\mathbf{c}_{\mathbf{m}_0})^{\alpha}$ are independent of $\mathbf{m}_0$ at the bifurcation point. It represents the projection of the second derivative of the first chemical moments $M_{\alpha}^{\alpha' \alpha''}$ on these eigenvectors. It is through this latter quantity that the second smallness parameter μ present in our problem-[cf. Eq. (18b)] is introduced. Explicit expressions are given in the next section devoted to the trimolecular model.

4.2. Quartic Terms

Utilizing Eqs. (9a) and (9b) at their steady state, switching to the representation diagonalizing U^{ij} and neglecting terms of higher order, both in μ and in the deviation $\lambda - \lambda_c$ from the bifurcation point, we obtain from (9c) an equation of the same form as (22b) which can be solved by inverting the operator ${}^{Q}H_i^h/\varepsilon_h$. If use is made of the expressions for ${}^{Q}U^{i_0 j_0 k}$ deduced in the first part of the present section, the coefficient of the quartic terms of the critical potential U_{cr} [Eq. (21)] takes the following form:

$$\begin{aligned}
&\bar{U}^{i_0 j_0 k_0 l_0} - \mathscr{S}_{i_0 j_0 k_0 l_0} \left\{ \sum_{h \neq h_0} \bar{U}^{i_0 j_0 h} \frac{1}{\varepsilon_h} \bar{U}^{h k_0 l_0} \right\} \\
&\quad = \bar{U}_{\text{cr}}^{i_0 j_0 k_0 l_0} = \mathscr{S}_{i_0 j_0 k_0 l_0} \left\{ \varepsilon_{i_0} \sum_h \frac{(\mathbf{Q}^{\bar{i}_0} \cdot \mathbf{C}^h)}{\omega_h} \right. \\
&\qquad \left. \times \left({}^{C}H_h^{j_0 k_0 l_0} - \sum_{h' \neq h_0'} {}^{C}H_h^{j_0 h'} \frac{1}{\omega_{h'}} {}^{C}H_{h'}^{k_0 l_0} \right) \right\}
\end{aligned} \tag{24}$$

This expression can be simplified by noting that the only nonvanishing contribution is for $h = i_0$ [see also discussion following Eqs. (23)]. Utilizing Eqs. (15) and (7) we thus obtain

$$\begin{aligned}
&\bar{U}_{\text{cr}}^{\mathbf{m}_0 \alpha_c \mathbf{m}_0' \alpha_c \mathbf{m}_0'' \alpha_c \mathbf{m}_0''' \alpha_c} \\
&\quad = -\frac{2}{l_c} \mathscr{S}_{\mathbf{m}_0 \mathbf{m}_0' \mathbf{m}_0''} \left\{ \gamma' - \sum_{\mathbf{m}\beta \neq \mathbf{m}_0 \alpha_c} \delta(\mathbf{m} + \mathbf{m}_0' + \mathbf{m}_0'') \Gamma^{\mathbf{m}\beta} \frac{1}{\omega_{\mathbf{m}\beta}} \Gamma_{\mathbf{m}\beta} \right\} \\
&\qquad \times \delta(\mathbf{m}_0 + \mathbf{m}_0' + \mathbf{m}_0'' + \mathbf{m}_0''')
\end{aligned} \tag{25a}$$

We have introduced one scalar quantity γ' and two vectorial quantities $\Gamma^{\mathbf{m}\beta}$, $\Gamma_{\mathbf{m}\beta}$, which represent projections of second and third derivatives of the first chemical transition moment on the eigenvectors $(\mathbf{c}_{\mathbf{m}})^{\alpha}$. They are similar to the scalar defined in the discussion following Eq. (23c), and which will be denoted by γ. The explicit expressions of these quantities are

$$\begin{aligned}
\gamma &= (c_{\mathbf{m}_c}^{-1})_{\alpha_c}^{\beta_1} M_{\beta_1}^{\beta_2 \beta_3} (c_{\mathbf{m}_c})_{\beta_2}^{\alpha_c} (c_{m_c})_{\beta_3}^{\alpha_c} \\
\gamma' &= (c_{\mathbf{m}_c}^{-1})_{\alpha_c}^{\beta_1} M_{\beta_1}^{\beta_2 \beta_3 \beta_4} (c_{\mathbf{m}_c})_{\beta_2}^{\alpha_c} (c_{\mathbf{m}_c})_{\beta_3}^{\alpha_c} (c_{\mathbf{m}_c})_{\beta_4}^{\alpha_c} \\
\Gamma^{\mathbf{m}\beta} &= (c_{\mathbf{m}_c}^{-1})_{\alpha_c}^{\beta_1} M_{\beta_1}^{\beta_2 \beta_3} (c_{\mathbf{m}_c})_{\beta_2}^{\alpha_c} (c_{\mathbf{m}})_{\beta_3}^{\beta} \\
\Gamma_{\mathbf{m}\beta} &= (c_{\mathbf{m}}^{-1})_{\beta}^{\beta_1} M_{\beta_1}^{\beta_2 \beta_3} (c_{\mathbf{m}_c})_{\beta_2}^{\alpha_c} (c_{\mathbf{m}_c})_{\beta_3}^{\alpha_c}
\end{aligned} \tag{25b}$$

5. APPLICATION TO THE BRUSSELATOR MODEL

In this section we analyze a specific example, corresponding to the following reaction scheme$^{(1)}$:

$$\mathrm{A} \xrightarrow{k_1} \mathrm{X}$$

$$2\mathrm{X} + \mathrm{Y} \xrightarrow{k_2} 3\mathrm{X}$$

$$\mathrm{B} + \mathrm{X} \xrightarrow{k_3} \mathrm{Y} + \mathrm{D}$$

$$\mathrm{X} \xrightarrow{k_4} \mathrm{E}$$

A is kept in excess, D and E are instantly removed, whereas X, Y are the two variable intermediates. The kinetic coefficients characterizing the chemical reactions are given in Table I, where use has been made of the standard change of variables incorporating most of k_ρs in suitable redefinitions of X, Y, A, B, and time scale.

The reference state used is the well-known uniform steady state solution:

$$\bar{x}_1 = a$$

$$\bar{x}_2 = \frac{b}{a}$$

In order to express the stochastic potential in the form given by Eq. (21) we have to evaluate (i) the eigenvalues and eigenvectors of the linearized stability operator $\mathscr{L}_i^j$, (ii) the eigenvalues and eigenvectors of U^{ij}, and (iii) the appropriate projections on the eigenvectors of $\mathscr{L}_i^j$ of the derivatives of the first chemical transition moment, i.e., γ, $\Gamma^{\mathrm{m}\alpha}$, $\Gamma_{\mathrm{m}\alpha}$, γ'.

For periodic boundary conditions, the eigenvectors of $\mathscr{L}_i^j$ are given by Eq. (11), where $(\mathbf{c}_\mathrm{m})^\alpha$ obeys Eq. (12). The latter takes the following matrix form for the trimolecular model:

$$\begin{pmatrix} b - 1 - K_\mathrm{m} D_1 - \omega_{\mathrm{m}\alpha} & a^2 \\ -b & -a^2 - K_\mathrm{m} D_2 - \omega_{\mathrm{m}\alpha} \end{pmatrix} \begin{pmatrix} (c_\mathrm{m})_1^\alpha \\ (c_\mathrm{m})_2^\alpha \end{pmatrix} = 0 \qquad (26\mathrm{a})$$

Table I

ρ	$\nu_{\rho 1}$	$\nu_{\rho 2}$	$\bar{\nu}_{\rho 1}$	$\bar{\nu}_{\rho 2}$	$\bar{k}_\rho$
1	1	0	0	0	a
2	1	−1	2	1	1
3	−1	1	1	0	b
4	−1	0	1	0	1

where we have set

$$K_{\mathbf{m}} = \frac{1}{2d} \sum_{\mathbf{a}} (1 - e^{i\mathbf{m}\cdot\mathbf{a}}) \tag{26b}$$

The eigenvalues $\omega_{\mathbf{m}1}$ and $\omega_{\mathbf{m}2}$ are the solutions of the solvability condition of the homogeneous system (26a) expressed by the characteristic equation. The bifurcation is marked by the vanishing of the largest of them, say, $\omega_{\mathbf{m}_c1}$. In a large system for which the spectrum of these eigenvalues is quasicontinuous, $\omega_{\mathbf{m}_c1}$ obeys both the characteristic equation of (26a) and a relation expressing that $\omega_{\mathbf{m}1}$ is a maximum for $\mathbf{m} = \mathbf{m}_c$:

$$(b - 1 - K_{\mathbf{m}} D_1 - \omega_{\mathbf{m}1})(-a^2 - K_{\mathbf{m}} D_2 - \omega_{\mathbf{m}1}) + a^2 b = 0 \tag{27a}$$

$$D_1(-a^2 - K_{\mathbf{m}} D_2 - \omega_{\mathbf{m}1}) + D_2(b - 1 - K_{\mathbf{m}} D_1 - \omega_{\mathbf{m}1}) = 0 \tag{27b}$$

At the bifurcation point, Eqs. (27a,b) admit the solution $\omega_{\mathbf{m}_c1} = 0$, which implies

$$b_c = (1 + a\eta)^2 \qquad \text{with} \quad \eta = \left(\frac{D_1}{D_2}\right)^{1/2} \tag{28a}$$

$$K_{\mathbf{m}_c} = \frac{a}{(D_1 D_2)^{1/2}} = K_c \tag{28b}$$

From Eqs. (28a,b) we easily deduce the dominant order of the normalized eigenvectors $(\mathbf{c}_{\mathbf{m}})^{\alpha_c}$ and then evaluate the scalars l_c, γ, γ', defined in Eqs. (15b, 25b). We find

$$l_c = \frac{4(1 + a\eta)}{a(1 - \eta^2)^2} [a^2 + \eta^2(1 + a\eta)^2] \tag{29a}$$

$$\gamma = -\frac{2(1 - a\eta)}{(1 - \eta^2)[a^2 + \eta^2(1 + a\eta)^2]^{1/2}} \tag{29b}$$

$$\gamma' = -\frac{6a\eta}{(1 - \eta^2)[a^2 + \eta^2(1 + a\eta)^2]} \tag{29c}$$

The results (28a) and (29b) allow us to choose the following small parameters which control both the deviation from the bifurcation point and the distance between simultaneously stable branches:

$$\lambda - \lambda_c = b - b_c$$

$$\mu = 1 - a\eta$$

Moreover, the vectorial quantity $\Gamma_{\mathbf{m}\beta}$ appearing in the expression (25a) for $\bar{U}_{\mathrm{cr}}^{i_0 j_0 k_0 l_0}$ can be shown to display the parameter μ as a multiplying factor. We find more explicitly

$$\Gamma_{\mathbf{m}\beta} = (1 - a\eta) \frac{2a(1 + a\eta)}{a^2 + \eta^2 (1 + a\eta)^2} \left[(c_{\mathbf{m}}^{-1})_{\beta}^{1} - (c_{\mathbf{m}}^{-1})_{\beta}^{2} \right] \tag{30}$$

As a result, for this model, the second term of the curly bracket in the expression (25a) is negligible to our order of approximation. The coefficients of the cubic and quartic terms of the expansion (21) reduce therefore, respectively, to $(-2\gamma/l_c)\,\delta(\mathbf{m}_0 + \mathbf{m}_0' + \mathbf{m}_0'')$ and $(-2\gamma'/l_c)\,\delta(\mathbf{m}_0 + \mathbf{m}_0' + \mathbf{m}_0'' + \mathbf{m}_0''')$.

We now have to evaluate the coefficients of quadratic terms ε_{i_0}, which are given, to dominant order, by Eq. (15a). More specifically, the perturbative method relating the eigenvalues of U_{ij}^{-1} and $\mathscr{L}$ gives the following result:

$$\varepsilon_{\mathbf{m}_0 \alpha_c} = -\frac{2}{l_{\mathbf{m}_0}} \omega_{\mathbf{m}_0 \alpha_c} + O(\varepsilon^2_{\mathbf{m}_0 \alpha_c}) \tag{31a}$$

with

$$l_{\mathbf{m}_0} = (c_{\mathbf{m}_0}^{-1})_{\alpha_c}^{\beta_1} (c_{\mathbf{m}_0}^{-1})_{\alpha_c}^{\beta_2} [M_{\beta_1 \beta_2} + 2\bar{x}_{\beta_1} (M_{\beta_2}^{\beta_1} - \omega_{\mathbf{m}_0 \alpha_c} \delta_{\beta_1 \beta_2})] \tag{31b}$$

Note that $\varepsilon_{\mathbf{m}_0 \alpha_c}$ depends then on the various parameters $\lambda, \mu, \ldots$ as well as on $\mathbf{m}_0$, the latter dependence entering through $K_{\mathbf{m}_0}$. When λ approaches λ_c, all the eigenvalues $\varepsilon_{\mathbf{m}_0 \alpha_c}$ become small inasmuch as the various values of $K_{\mathbf{m}_0}$ are close together (and close to K_c). In the general case, the $K_{\mathbf{m}_0}$ dependence of $\omega_{\mathbf{m}_0 \alpha_c}$ and $(\mathbf{c}_{\mathbf{m}_0})^{\alpha_c}$ can be expressed with the help of a perturbative technique. For a given model as the Brusselator, we can expand $\omega_{\mathbf{m}_0 \alpha_c}$ and $l_{\mathbf{m}_0}$ in Taylor series in terms of the two variables $b - b_c$ and $K_{\mathbf{m}_0} - K_c$, assuming that $K_{\mathbf{m}_0}$ is continuous for a large system. Because of the definition of b_c and K_c, the dominant terms in the expansions of $\omega_{\mathbf{m}_0 \alpha_c}$ and $\varepsilon_{\mathbf{m}_0 \alpha_c}$ are of order $(b - b_c)$ and $(K_{\mathbf{m}_0} - K_c)^2$. Moreover, in order to determine the wave vector (or $K_{\mathbf{m}_0}$) which gives to $\omega_{\mathbf{m}_0 \alpha_c}$ or $\varepsilon_{\mathbf{m}_0 \alpha_c}$ its extremum value, for conditions which are slightly different from critical ones ($b - b_c \neq 0$), we keep in these expansions the terms of order $(b - b_c)(K_{\mathbf{m}_0} - K_c)$. We thus obtain

$$\omega_{\mathbf{m}_0 \alpha_c} = \frac{1}{(1 + a\eta)(1 - \eta^2)} \left[b - b_c + \frac{a\eta(1 - \eta^2) - 2\eta^2}{(1 + a\eta)(1 - \eta^2)} \times (b - b_c) \frac{K_{\mathbf{m}_0} - K_c}{K_c} - a\eta \left(\frac{K_{\mathbf{m}_0} - K_c}{K_c} \right)^2 \right] \tag{32a}$$

$$\varepsilon_{\mathbf{m}_0\alpha_c} = -\frac{a(1-\eta^2)}{2(1+a\eta)^2[a^2+\eta^2(1+a\eta)^2]} \times \left[b - b_c + \frac{2\eta^2[a^2+(1+a\eta)^2]}{(1-\eta^2)(1+a\eta)[a^2+\eta^2(1+a\eta)^2]} \times (b-b_c)\frac{K_{\mathbf{m}_0}-K_c}{K_c} - a\eta\left(\frac{K_{\mathbf{m}_0}-K_c}{K_c}\right)^2\right] \tag{32b}$$

Summarizing, for small values of the parameters $(b-b_c)$ and $(1-a\eta)$, the stochastic potential of the trimolecular model takes the following form, restricted to the critical mode contribution:

$$U_{\mathrm{cr}} = n\left(\frac{1}{2}\sum_{\mathbf{m}_0} \varepsilon_{\mathbf{m}_0\alpha_c} |\zeta_{\mathbf{m}_0\alpha_c}|^2 - \frac{\gamma}{3l_c}\sum_{\mathbf{m}_0\mathbf{m}_0'\mathbf{m}_0''} \delta(\mathbf{m}_0+\mathbf{m}_0'+\mathbf{m}_0'')\,\zeta_{\mathbf{m}_0\alpha_c}\zeta_{\mathbf{m}_0'\alpha_c}\zeta_{\mathbf{m}_0''\alpha_c} - \frac{\gamma'}{12l_c}\sum_{\mathbf{m}_0\mathbf{m}_0'\mathbf{m}_0''\mathbf{m}_0'''} \delta(\mathbf{m}_0+\mathbf{m}_0'+\mathbf{m}_0''+\mathbf{m}_0''')\,\zeta_{\mathbf{m}_0\alpha_c}\zeta_{\mathbf{m}_0'\alpha_c}\zeta_{\mathbf{m}_0''\alpha_c}\zeta_{\mathbf{m}_0'''\alpha_c}\right) \tag{33}$$

where l_c, γ, γ' are given by (29) and $\varepsilon_{\mathbf{m}_0\alpha_c}$ by (32b).

The transformed variables $\zeta_{\mathbf{m}_0\alpha_c} = \zeta_{\mathbf{m}_0 1}$, defined in Eq. (16), can be easily expressed in terms of the discrete Fourier transforms of the initial variables: $\bar{\xi}_{\mathbf{m}\alpha} = (1/\sqrt{n})\sum_{\mathbf{r}} \exp(i\mathbf{m}\cdot\mathbf{r})\,\xi_{\mathbf{r}\alpha}$. Using Eqs. (11), (15a), (16), we obtain, for the trimolecular model,

$$\zeta_{\mathbf{m}_0 1} = -\frac{1}{\sqrt{n}}\frac{[a^2+\eta^2(1+a\eta)^2]^{1/2}}{a}\bar{\xi}_{\mathbf{m}_0 1} = \frac{1}{\sqrt{n}}\frac{[a^2+\eta^2(1+a\eta)^2]^{1/2}}{(1+a\eta)}\bar{\xi}_{\mathbf{m}_0 2} \tag{34}$$

The stochastic potential (33) has thus the same structure as the Brazovskii potential obtained by Walgraef *et al.*,$^{(6)}$ at the dominant order in $(b-b_c)$ and $(1-a\eta)$. In fact, if one requires complete identity of the results to that order, one has a way to compute the strength of the random force, Γ_L, which is added to the phenomenological equations in Ref. 6, and which is assumed to obey a fluctuation-dissapation theorem. The result is

$$\Gamma_L = \frac{2\eta^2}{a}(1+a\eta) \tag{35}$$

Having reduced the probability distribution to the exponential of a Brazovskii-type potential, one may apply the techniques of critical phenomena to evaluate the deviations from the mean-field theory arising from the fluctuations, particularly in two dimensions. We refer to Walgraef *et al.*$^{(6)}$ for a discussion of this point.

Note that in the Brazovskii potential given in Ref. 6, certain wave-vector-dependent terms have been retained in the quartic terms by Walgraef *et al.* Within the framework of a perturbative approach, these terms are proportional to the small parameter $(1 - a\eta)$ and must then be neglected in order to preserve the consistency of the expansion procedure. It is worthwhile to note however that in the general case, the coefficients of the quartic terms of our expansion may well contain a wave-vector-dependent part [see Eq. (25a)]. For the trimolecular model, this part, of order $(1 - a\eta)$, is identical to the wave-vector-dependent term obtained in Ref. 6.

Note finally that we have retained in the expression (32b) of the coefficient of the quadratic component of U, terms of order $(b - b_c)(K_{\mathbf{m}_0} - K_c)$ which are small compared to those of order $(b - b_c)$ and ought to be neglected in a perturbative approach. However, these terms introduce a new qualitative effect as they allow us to determine, to the first order in $(b - b_c)$, the value K_0 of $K_{\mathbf{m}_0}$ which gives to $\varepsilon_{\mathbf{m}_0 \alpha_c}$ its smallest value. From Eq. (32b) we find

$$K_0 = K_c \left(1 + \frac{\eta}{a} \frac{a^2 + (1 + a\eta)^2}{(1 - \eta^2)(1 + a\eta)[a^2 + \eta^2(1 + a\eta)^2]} (b - b_c)\right) \qquad (36)$$

The corresponding modes are expected to play the dominant role in the description of the spatial structures arising through bifurcation. We see that K_0 increases with respect to K_c for $b > b_c$, and decreases for $b < b_c$. Alternatively, the wavelength of the structure decreases or increases according to whether one is, respectively, above or below the bifurcation point. Now, in a variety of systems ranging from Bénard instability to crystal growth,$^{(12)}$ an increase of wavelength is observed. Our result is compatible with such a tendency if the dominant structure (in the sense of the most probable state) first arises in the subcritical region. We have therefore the beginning of an answer to mode selection. It should be realized however that, strictly speaking, Eq. (36) is beyond the validity of the perturbative approach utilized throughout our paper.

6. DISCUSSION

We believe that the results obtained in the present paper provide new insights on two problems of interest in the study of nonequilibrium phenomena: the connection between deterministic (Brazovskii) and stochastic potentials associated with symmetry-breaking bifurcations and the behavior of fluctuations near the confluence of two different singularities.

We have shown that in a general reaction-diffusion system, a stochastic potential restricted to the critical modes can be derived. In this respect, therefore, the Brazovskii potential is recovered. It is to be noted however that, in general, the coefficient of the quartic term depends on the noncritical wave vectors. Interestingly, in the Brusselator model this contribution is small near the coalescence of the bifurcation and the limit points ($\lambda \to \lambda_c$, $\mu \to 0$). It would be important to extend these results to models involving more than two variables as well as to other symmetry-breaking transitions, particularly those leading to time-periodic inhomogeneous solutions.

Throughout the analysis we have insisted on the importance of ensuring consistency between the terms kept in the stochastic potential on the one side, and the parameters controlling the transitions occurring in the deterministic equations of evolution on the other side. We have seen that the use of the bifurcation parameter alone was not sufficient to achieve this purpose. We therefore concluded that it was necessary to study the behavior of fluctuations in the nearly degenerate situation in which the singularity associated with the bifurcation point was close to that associated with the limit point. In this way the range of validity of the stochastic potential could be determined unambiguously. We believe that a similar procedure should apply to the study of the stochastic aspects of higher codimension bifurcations, which attracted considerable attention recently.(13)

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