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Systematic Analysis of the Multivariate Master Equation for a Reaction–Diffusion System

G. Nicolis[1] **and M. Malek-Mansour**[1,2]

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The multivariate master equation for a reaction–diffusion system is analyzed using a singular perturbation approach. It is shown that in the vicinity of a bifurcation leading to two simultaneously stable steady states, the steady-state probability distribution reduces asymptotically to the exponential of the Landau–Ginzburg functional. On the other hand, for a system displaying quadratic nonlinearities and an absorbing state, critical behavior is ruled out.

KEY WORDS: Master equations; reaction–diffusion systems; chemical instabilities; nonequilibrium phase transitions.

1. INTRODUCTION

Systems involving chemical reactions and diffusion give rise to a considerable variety of solutions arising via a bifurcation mechanism far from thermodynamic equilibrium.[(1)] The simplest situation of this kind involves the first bifurcation from a uniform steady-state solution. As is well known, it may lead either to spatially uniform multiple steady states or to symmetry breaking associated with the emergence of spatial dissipative structures or of limit cycles.

Several authors have attempted an analysis of the fluctuations in the vicinity of these bifurcation phenomena.[(1,2)] Broadly speaking, these analyses can be classified into two different categories as follows.

1.1. The Master Equation Approach

Let $\{\bar{x}_i\}$ denote the (macroscopically measured) concentrations of the active chemical intermediates. Assuming Fickian diffusion in a dilute mixture

[1] Faculté des Sciences, Université Libre de Bruxelles, Brussels, Belgium.

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and constant temperature throughout, the phenomenological evolution equations of these variables take the form

$$\partial \bar{x}_i/\partial t = v_i(\bar{x}_1,\ldots,\bar{x}_n;\lambda) + \mathscr{D}_i \nabla^2 \bar{x}_i \tag{1.1}$$

The $\mathscr{D}_i$ are diffusion coefficients, v_i is the overall rate of change of $\bar{x}_i$ arising from the chemical reactions involving constituent i, and λ stands for a set of parameters descriptive of the system (among which one may choose the bifurcation parameter).

The main idea behind the master equation approach is to appeal *explicitly* to the chemical and diffusion mechanisms underlying Eq. (1.1) and to construct a Markov process in an appropriate phase space. The usual rules for constructing this process are to model diffusion as a *random walk* between adjacent spatial cells $\mathbf{r}$, and to view chemical reactions as *birth and death processes* corresponding to the appearance or disappearance of a small number of molecules (usually one) at a time. One writes in this way the *multivariate master equation*:

$$\begin{aligned}\frac{dP(\{X_{i\mathbf{r}}\},t)}{dt} = \sum_{\mathbf{r}}\Bigg\{&\sum_{\{X'_{i\mathbf{r}}\}} W(\{X'_{i\mathbf{r}}\}|\{X_{i\mathbf{r}}\})P(\{X'_{i\mathbf{r}}\},t)\\ &+\sum_{\boldsymbol{\lambda},i}\frac{D_i}{2d}[(X_{i\mathbf{r}}+1)P(X_{i,\mathbf{r}+\mathbf{r}}-1, X_{i\mathbf{r}}+1,\{X'_{i\mathbf{r}}\},t)\\ &- X_{i\mathbf{r}}P(\{X_{i\mathbf{r}}\},t)]\Bigg\}\end{aligned} \tag{1.2}$$

$\{X_{i\mathbf{r}}\}$ denotes the number of particles of species i in cell $\mathbf{r}$, the D_i are the diffusion rates across cells, d is the spatial dimensionality, $\boldsymbol{\lambda}$ denotes the first neighbors of cell $\mathbf{r}$, and W is the transition probability per unit time for the chemical processes. Among the constraints that enable us to assign a unique structure to W, we cite the requirement that at thermodynamic equilibrium $P(\{X_{i\mathbf{r}}\},t)$ should become multi-Poissonian (multinomial in a closed system), and that one should recover Eq. (1.1) as the time evolution of the average value in the absence of bifurcation.

Equation (1.2) confronts us with an extremely complex problem. For this reason, the only results obtained so far are based either on mean-field hypotheses, neglecting the effect of spatial fluctuations,[3–8] or on truncation of the hierarchy of moment equations to second order.[1,9–11] In either case, one predicts classical values of the critical exponents describing the divergence of the variance and of the correlation length on approaching the bifurcation point.

Despite the absence of a clear-cut perturbation parameter associated with the above approximations, certain authors[11,12] attempted to determine critical dimensionalities beyond which mean-field theories or truncation procedures would be qualitatively correct. As we see later, however, in the vicinity of the bifurcation point the various parts of Eq. (1.2) are so intricately coupled that all straightforward perturbation expansions are bound to fail.

1.2. The Critical Dynamics Approach

The rather unsatisfactory status of the above analyses prompted some authors [13–15] to suggest a different approach, based on the use of renormalization group techniques. These methods amount to adding appropriately correlated Langevin forces [2,16] to the right-hand sides of the balance equations (1.1) and analyzing diagrammatically the resulting stochastic differential equations. For systems involving multiple steady states without symmetry breaking they often lead to time-dependent Landau–Ginzburg models. Hence, one obtains nonclassical exponents describing the law of divergence of the various quantities as well as critical dimensionalities higher than $d = 3$. These results rest entirely on the structure of the nonlinear equations (1.1), and are otherwise *independent* of the more detailed nature of the chemical system under consideration.

We believe that a more satisfactory approach to fluctuations in reaction–diffusion systems should utilize, at least at the beginning of the analysis, the maximum amount of specific information pertaining to the system. Such is the case of the multivariate master equation (1.2). It may happen, of course, that in the vicinity of bifurcation, much of this information becomes irrelevant. One could thus be led to results similar to the renormalization group results. However, instead of postulating a priori a universal behavior, one would have information on the conditions making such a universality possible.

Naturally, such a program implies that one can set up a *systematic* analysis of the master equation (1.2). This is the object of the present paper, for the particular family of systems admitting multiple steady-state transitions without symmetry-breaking. In Section 2 we introduce the Schlögl model, which is the prototype of such systems, and write down the multivariate master equation for an arbitrary dimensionality. Section 3 is devoted to a singular perturbative solution of this equation at the steady state in the generating function representation. After showing the failure of all naive perturbative expansions, we obtain, to zeroth order of our scheme, an equation whose steady-state solution reduces to the exponential of the Landau–Ginzburg functional. This establishes the connection between master-equation and renormalization-group approaches. In Section 4 we discuss higher approximations as well as the asymmetric (nonzero-"field") bifurcation case. In Section 5 we consider a model involving bifurcation of a nontrivial branch from a trivial ($\bar{x} = 0$) reference state. We show that this system cannot admit a nonequilibrium phase transition, due to the existence of an absorbing state. Some comments on the implications of the results are made in Section 6.

2. MULTIVARIATE MASTER EQUATION FOR THE CUSP BIFURCATION. SCHLÖGL'S MODEL

The simplest bifurcation leading to multiple steady states without symmetry breaking is in systems involving one concentration variable and a cubic rate law. This is best illustrated by the following chemical model due to Schlögl[17]:

$$\begin{gathered} \mathrm{A} + 2\mathrm{X} \underset{k_2}{\overset{k_1}{\rightleftarrows}} 3\mathrm{X} \\ \mathrm{X} \underset{k_4}{\overset{k_3}{\rightleftarrows}} \mathrm{B} \end{gathered} \tag{2.1}$$

where A, B are controlled from outside and, in general, $\bar{x}_A/\bar{x}_B \neq k_2k_4/k_1k_3$. As is well known, the behavior of a cubic system is controlled by two parameters. Hence, on defining the scaled quantities

$$\begin{gathered} \bar{x}_{\mathbf{r}} = \bar{X}_{\mathbf{r}}/\Delta V = (1 + \bar{\sigma}_{\mathbf{r}}), \qquad k_1A/k_2 = 3\,\Delta V, \qquad k_3/k_2 = (3 + \delta) \\ k_4B/k_2 = (1 + \delta')\,\Delta V, \qquad \tau = k_2 t, \qquad \bar{\mathscr{D}} = \mathscr{D}_x/k_2 \end{gathered} \tag{2.2}$$

where A and B are the numbers of particles of A and B and ΔV is the size of the spatial cell centered on $\mathbf{r}$, we may write the following rate equation for model (2.1):

$$\partial\bar{\sigma}_{\mathbf{r}}/\partial\tau = -\bar{\sigma}_{\mathbf{r}}^3 - \delta\bar{\sigma}_{\mathbf{r}} + (\delta' - \delta) + \bar{\mathscr{D}}\,\nabla^2\bar{\sigma}_{\mathbf{r}} \tag{2.3}$$

As is well known, for natural boundary conditions (infinite systems or periodic geometry), the diffusion term does not add new stable solutions to Eq. (2.3) in the vicinity of the cusp bifurcation $\delta = \delta' = 0$. Thus, as δ, δ' move to negative values along the line $\delta = \delta'$, a bifurcation of *uniform* steady-state solutions $\bar{\sigma}_{\mathbf{r}} \equiv \bar{\sigma}_{\pm} = \pm\sqrt{-\delta}$ takes place from the trivial solution $\bar{\sigma}_0 = 0$. If, on the other hand, one moves into the multiple steady-state region for $\delta \neq \delta'$, one encounters the phenomenon of hysteresis.

We now want to analyze the behavior of fluctuations associated with the above-mentioned transition phenomena. To this end, we write Eq. (1.2) directly in the generating function representation

$$F(\{s_{\mathbf{r}}\}, t) = \sum_{\{X_{\mathbf{r}}\}} \prod_{\mathbf{r}} S_{\mathbf{r}}^{X_{\mathbf{r}}} P(\{X_{\mathbf{r}}\}, t) \tag{2.4}$$

Taking into account the extensivity of the transition probabilities and setting $D_x = D$ we obtain, at the steady state

$$\begin{aligned} &\sum_{\mathbf{r}} (1 - S_{\mathbf{r}})S_{\mathbf{r}}^2\left(\frac{1}{\Delta V^2}\frac{\partial^3 F}{\partial S_{\mathbf{r}}^3} - 3\frac{1}{\Delta V}\frac{\partial^2 F}{\partial S_{\mathbf{r}}^2}\right) \\ &\quad + \sum_{\mathbf{r}} (1 - S_{\mathbf{r}})\left[(3 + \delta)\frac{\partial F}{\partial S_{\mathbf{r}}} - (1 + \delta')\,\Delta V F\right] \\ &\quad + \frac{D}{2d}\sum_{\mathbf{r}\lambda} (S_{\mathbf{r}+\lambda} - S_{\mathbf{r}})\frac{\partial F}{\partial S_{\mathbf{r}}} = 0 \end{aligned} \tag{2.5}$$

As is well known, F generates all moments of the probability distribution, including the average value, which satisfies the macroscopic rate equation (2.3), at least before bifurcation, where the system admits a single steady state. In order to sort out the information pertaining more specifically to the fluctuations, it will be convenient to extract from Eq. (2.5) the macroscopic part[3] by setting

$$F = \prod_{\mathbf{r}} \left\{ \exp[\Delta V \bar{x}_{\mathbf{r}}(S_{\mathbf{r}} - 1)] \right\} \psi \tag{2.6a}$$

In much of this paper we will be interested in the symmetric bifurcation case, $\delta = \delta'$. As is seen from Eqs. (2.2) and (2.3), one has then $\bar{x}_{\mathbf{r}} = 1$ and Eq. (2.6a) becomes

$$F = \left\{ \exp\left[\Delta V \sum_{\mathbf{r}} (S_{\mathbf{r}} - 1) \right] \right\} \psi \qquad (\delta = \delta' \gg 0) \tag{2.6b}$$

Substituting into Eq. (2.5), we obtain

$$\begin{aligned} &\sum_{\mathbf{r}} (1 - S_{\mathbf{r}}) S_{\mathbf{r}}^2 \left(-2\,\Delta V \psi - 3 \frac{\partial \psi}{\partial S_{\mathbf{r}}} + \frac{1}{\Delta V^2} \frac{\partial^3 \psi}{\partial S_{\mathbf{r}}^3} \right) \\ &\quad + \sum_{\mathbf{r}} (1 - S_{\mathbf{r}}) \left[2\,\Delta V \psi + (3 + \delta) \frac{\partial \psi}{\partial S_{\mathbf{r}}} \right] \\ &\quad - \frac{D}{2d} \sum_{\mathbf{r}\lambda} (1 - S_{\mathbf{r}}) \left(\frac{\partial \psi}{\partial S_{\mathbf{r}+\lambda}} - \frac{\partial \psi}{\partial S_{\mathbf{r}}} \right) \end{aligned} \tag{2.7}$$

with

$$\psi(\{S_{\mathbf{r}} = 1\}) = 1, \qquad \left. \frac{\partial \psi}{\partial S_{\mathbf{r}}} \right|_{\{S_{\mathbf{r}} = 1\}} = o(1) \tag{2.8}$$

where the smallness parameter appearing in $o(1)$ is the inverse of the volume ΔV (see also Section 3). Note the cancellation of the second derivative terms in this equation and the transformation of the diffusion operator into a form displaying the factor $(1 - S_{\mathbf{r}})$ in front of the first derivatives.

3. SINGULAR PERTURBATION ANALYSIS

In order to analyze Eq. (2.7) systematically, we need some asymptotic element enabling us to set up a perturbative procedure. At first sight, one is struck by the absence of any perturbation parameter in the problem. Indeed, the distance δ from the bifurcation point appears in a very implicit manner. Moreover, although the diffusion rate D is typically much larger than the chemical rate constants, it turns out that it cannot be used as a perturbation

[3] Note that this implies the validity of the law of large numbers for the reaction–diffusion system. This point was recently investigated in Ref. 18a.

parameter, since it leads to expansions which diverge term by term in the thermodynamic limit.[22]

An answer to this difficulty can be found by *anticipating* the existence of a nonequilibrium transition. In this case, because of the long-range character of the correlations between spatial cells, we expect to be able to augment ΔV until it reaches macroscopic dimensions.[19] Hence, near the bifurcation point we set

$$\epsilon = 1/\Delta V \ll 1 \qquad \text{with} \qquad \delta = \epsilon^b \delta_1 + \cdots \tag{3.1}$$

The second asymptotic element is found by realizing that all macroscopically relevant information refers to the vicinity of $\{S_{\mathbf{r}} = 1\}$. This information is expected to be closer to the solutions of the phenomenological equation (2.3) the larger the ΔV. Moreover, it is reasonable to require the thermodynamic limit to be taken *before* the limit $\{S_{\mathbf{r}} \to 1\}$.[4] Hence, we scale the deviation of $S_{\mathbf{r}}$ from 1 by a suitable power of ϵ (to be determined later; see Ref. 6):

$$S_{\mathbf{r}} = 1 + \epsilon^a \xi_{\mathbf{r}}, \qquad 0 < a < 1 \tag{3.2a}$$

The physical meaning of this scaling can be realized if one starts from definition (2.4) and replaces, by virtue of Eq. (3.1), the sum over $\{X_{\mathbf{r}}\}$ by an integral using the Euler–McLaurin asymptotic formula. One can then show that Eq. (3.2a) in conjunction with Eq. (2.6a) amounts to studying the probability distribution of the scaled variable[8]

$$z = \frac{X - \Delta V \bar{x}}{\bar{x} \Delta V^a} \tag{3.2b}$$

Equation (2.7) becomes

$$\begin{aligned}
&\sum_{\mathbf{r}} -\xi_{\mathbf{r}}(1 + 2\epsilon^a \xi_{\mathbf{r}} + \epsilon^{2a}\xi_{\mathbf{r}}^2)\epsilon^{-2a+2} \frac{\partial^3 \psi}{\partial \xi_{\mathbf{r}}^3} \\
&\quad + \sum_{\mathbf{r}} -\xi_{\mathbf{r}}(2\epsilon^a \xi_{\mathbf{r}} + \epsilon^{2a}\xi_{\mathbf{r}}^2)\left(-2\epsilon^{-1+a}\psi - 3\frac{\partial \psi}{\partial \xi_{\mathbf{r}}}\right) \\
&\quad + \sum_{\mathbf{r}} -\xi_{\mathbf{r}}\, \delta \frac{\partial \psi}{\partial \xi_{\mathbf{r}}} \\
&\quad + \frac{D}{2d}\sum_{\mathbf{r}\lambda} \xi_{\mathbf{r}}\left(\frac{\partial \psi}{\partial \xi_{\mathbf{r}+\lambda}} - \frac{\partial \psi}{\partial \xi_{\mathbf{r}}}\right) = 0
\end{aligned} \tag{3.3}$$

To proceed further we need to scale the diffusion term. This scaling can easily be understood if one realizes that in actual fact, the double sum $\sum_{\mathbf{r}\lambda}$ in Eq. (3.3) displays the eigenvalues $\lambda_{\mathbf{r}}$ of the diffusion operator in the cell representa-

[4] If the two limits are taken simultaneously one obtains a probability distribution in the form of a delta function centered on the deterministic stable state.[6]

tion. Among these, one has the "low-lying" ones representing long-wavelength excitations, which are inversely proportional to the square of the number of cells.[20] For convenience we absorb this smallness factor into the proportionality coefficient D, Eq. (3.3). The overall effect of diffusion can now be scaled as follows:

$$D = \epsilon^f D_1 + \cdots \tag{3.4}$$

On inspecting Eqs. (3.1)–(3.4) we can see how different regimes corresponding to different choices of a, b, f can be realized. Thus, for

$$f > \max\{b, 2(1-a), 2a-1\}, \qquad b = 2(1-a) = 2a-1 \tag{3.5a}$$

one obtains the mean-field theory,[6] which neglects spatial fluctuations, to zeroth order of the perturbation analysis. On the other hand, for

$$f < \min\{b, 2(1-a), 2a-1\} \tag{3.5b}$$

one would have diffusion as the dominant part and chemical reactions as a "perturbation," as suggested some time ago by Van den Broeck *et al.*[20] Finally, the choice $2(1-a) > 2a-1$, or

$$a < \tfrac{3}{4} \qquad \text{and} \qquad 2a-1 = b = f \tag{3.5c}$$

gives

$$\sum_{\mathbf{r}} \xi_{\mathbf{r}} \left[\delta \frac{\partial \psi}{\partial \xi_{\mathbf{r}}} - \frac{D}{2d} \sum_{\boldsymbol{\lambda}} \left(\frac{\partial \psi}{\partial \xi_{\mathbf{r}+\boldsymbol{\lambda}}} - \frac{\partial \psi}{\partial \xi_{\mathbf{r}}} \right) \right] = \epsilon^{2a-1} \sum_{\mathbf{r}} 4\xi_{\mathbf{r}}^2 \psi \tag{3.6}$$

This yields the Gaussian approximation, as can be verified straightforwardly by switching to the cumulant generating function w:

$$\psi = \exp \frac{1}{\epsilon} w \tag{3.7}$$

We see therefore that the Gaussian is a legitimate representation of the system if a is small enough or, according to the second relation (3.5c), if the system is sufficiently far from the bifurcation point. This is compatible with the Ginzburg criterion familiar from the theory of phase transitions.[19]

Now, the difficulty with the reasoning leading to Eqs. (3.5)–(3.7) is that sufficiently close to the bifurcation point, the higher order terms of the perturbation expansion diverge,[11,22] at least for physically reasonable dimensionalities. One could try to get out of this difficulty by following the ideas of the theory of critical phenomena.[19] For instance, one cannot exclude the possibility of a suitable partial resummation scheme which would regularize the perturbation series in the vicinity of some critical dimensionality d_c. In the absence of such a result, we shall adopt an alternative procedure. Namely, we will develop a singular perturbation which enables us to keep, to lowest order in the expansion parameter ϵ, both diffusion and chemical reaction including the highest derivative term $\partial^3\psi/\partial\xi_{\mathbf{r}}^3$, which is missing in the Gaussian approximation, Eq. (3.6). According to Eq. (3.3), this corresponds to

$$2(1-a) = 2a - 1 = b = f \quad \text{or} \quad a = \tfrac{3}{4} \text{ and } b = f = \tfrac{1}{2} \tag{3.8}$$

Calling $\psi^{(0)}$ the lowest order approximation to ψ, we obtain

$$\sum_{\mathbf{r}} \xi_{\mathbf{r}} \left[\frac{\partial^3\psi^{(0)}}{\partial\xi_{\mathbf{r}}^3} + \delta_1 \frac{\partial\psi^{(0)}}{\partial\xi_{\mathbf{r}}} - \frac{D_1}{2d} \sum_{\boldsymbol{\lambda}} \left(\frac{\partial\psi^{(0)}}{\partial\xi_{\mathbf{r}+\boldsymbol{\lambda}}} - \frac{\partial\psi^{(0)}}{\partial\xi_{\mathbf{r}}} \right) \right] = 4 \sum_{\mathbf{r}} \xi_{\mathbf{r}}^2 \psi^{(0)} \tag{3.9}$$

We now seek for "detailed balance" solutions of this equation, by identifying the coefficients of $\xi_{\mathbf{r}}$ on both sides. We obtain

$$\frac{\partial^3\psi^{(0)}}{\partial\xi_{\mathbf{r}}^3} + \delta_1 \frac{\partial\psi^{(0)}}{\partial\xi_{\mathbf{r}}} - \frac{D_1}{2d} \sum_{\boldsymbol{\lambda}} \left(\frac{\partial\psi^{(0)}}{\partial\xi_{\mathbf{r}+\boldsymbol{\lambda}}} - \frac{\partial\psi^{(0)}}{\partial\xi_{\mathbf{r}}} \right) = 4\xi_{\mathbf{r}}\psi^{(0)} \tag{3.10}$$

To solve this equation we perform a Mellin–Fourier transform[5]:

$$\psi(\{\xi_{\mathbf{r}}\}) = \int_{-\infty}^{\infty} \cdots \int_{-\infty}^{\infty} \{d\theta_{\mathbf{r}}\} \left[\exp\left(\sum_{\mathbf{r}} \xi_{\mathbf{r}}\theta_{\mathbf{r}} \right) \right] R(\{\theta_{\mathbf{r}}\}) \tag{3.11}$$

where it is assumed that R goes to zero faster than exponentially when $|\theta_{\mathbf{r}}| \to \infty$. We obtain

$$-4 \frac{\partial R^{(0)}}{\partial\theta_{\mathbf{r}}} = (\theta_{\mathbf{r}}^3 + \delta_1\theta_{\mathbf{r}})R^{(0)} - \frac{D_1}{2d} \sum_{\boldsymbol{\lambda}} (\theta_{\mathbf{r}+\boldsymbol{\lambda}} - \theta_{\mathbf{r}})R^{(0)} \tag{3.12}$$

The solution of Eq. (3.12) is (up to a normalization factor Z^{-1})

$$R^{(0)} = Z^{-1} \exp \frac{-1}{4} \sum_{\mathbf{r}} \left[\delta_1 \frac{\theta_{\mathbf{r}}^2}{2} + \frac{\theta_{\mathbf{r}}^4}{4} + \frac{D_1}{8d} \sum_{\boldsymbol{\lambda}} (\theta_{\mathbf{r}+\boldsymbol{\lambda}} - \theta_{\mathbf{r}})^2 \right] \tag{3.13}$$

It will be noticed that in the continuum limit, Eq. (3.13) displays *the exponential of the Landau–Ginzburg functional*[13,19] expressed in terms of the *fluctuations* around the deterministic value $\bar{x}_{\mathbf{r}} = 1$. We have therefore established in this way the connection between master equations and the theory of critical phenomena.

From Eqs. (3.11) and (3.13) one can generate successive moments of the probability distribution. For instance, the doublet concentration correlation function

$$G(\mathbf{r}, \mathbf{r}') = \epsilon^2 \frac{\partial^2\psi}{\partial S_{\mathbf{r}}\,\partial S_{\mathbf{r}'}} \bigg|_{\{S_{\mathbf{r}}=1\}} = \epsilon^{2(1-a)} \frac{\partial^2\psi}{\partial\xi_{\mathbf{r}}\,\partial\xi_{\mathbf{r}'}} \bigg|_{\{\xi_{\mathbf{r}}=0\}} \tag{3.14}$$

becomes

$$G(\mathbf{r}, \mathbf{r}') = \int_{-\infty}^{\infty} \cdots \int_{-\infty}^{\infty} \{d\theta_{\mathbf{r}}\}\, \epsilon^{2(1-a)}\theta_{\mathbf{r}}\theta_{\mathbf{r}'}, R^{(0)}(\{\theta_{\mathbf{r}}\})$$

[5] Note the analogy with the Poisson representation developed by Gardiner and Chaturvedi[11].

Introducing the reduced variables $k_{\mathbf{r}} = \theta_{\mathbf{r}}\epsilon^{1/4}$ and eliminating δ_1, D_1 in favor of δ, D from Eq. (3.4), we obtain

$$G(\mathbf{r}, \mathbf{r}') = Z^{-1}\int_{-\infty}^{\infty} \cdots \int_{-\infty}^{\infty} \{dk_{\mathbf{r}}\}\, k_{\mathbf{r}}k_{\mathbf{r}'} \exp\left\{-\frac{1}{4}\sum_{\mathbf{r}} \epsilon^{-1} \times \left[\delta \frac{k_{\mathbf{r}}^2}{2} + \frac{k_{\mathbf{r}}^4}{4} + \frac{D}{8d}\sum_{\boldsymbol{\lambda}} (k_{\mathbf{r}+\boldsymbol{\lambda}} - k_{\mathbf{r}})^2\right]\right\} \tag{3.15}$$

Note that $\sum_{\mathbf{r}}\epsilon^{-1}$ is going to be transformed, in the continuum limit, into the space integral over the entire system.

The relation between Eqs. (3.15) and (3.13) further substantiates the physical meaning of the scaling introduced in Eq. (3.2a). Indeed, applying Eq. (3.2b) for $a = 3/4$ [cf. Eq. (3.8)], we have

$$z = \frac{\Delta V(x - \bar{x})}{\bar{x}\,\Delta V^a} = \frac{x - \bar{x}}{\bar{x}}\,\epsilon^{-1/4} \tag{3.16}$$

which is precisely the relation between the (intensive) variable k and the (scaled) variable θ.

Equation (3.15) can now be studied by renormalization group methods[13,19] as applied to the Ising model.[6] As is well known, the result of the analysis is the existence of a critical dimensionality $d_c = 4$, and the concomitant appearance of nonclassical exponents describing the divergence of variances, correlation functions, and so forth.

From the standpoint of probability theory, the results derived in the present section show that in the presence of diffusion, the asymptotic limit of the stochastic process described by the multivariate master equation is *not* given by the Gaussian distribution, even before (but close to) the bifurcation point. According to renormalization group theory,[19] the latter can only hold when the dimensionality is higher than four. The situation is therefore radically different from the behavior of birth and death processes and many other familiar processes involving a finite number of variables.[18b] On the other hand, the law of large numbers appears to be secured whatever the dimensionality of space, at least for any finite (but possibly very long) value of time.[18a]

4. HIGHER ORDER APPROXIMATIONS. THE NONZERO "FIELD" CASE, $\delta \neq \delta'$

One of the advantages of the master equation approach and of the perturbative method developed in Section 3 is the generation in a natural

[6] It should be pointed out that in our analysis (see also Ref. 13) the quartic term arises in a natural way from the nonlinearities of the system. This is to be contrasted with certain situations encountered in critical phenomena, where this term is merely introduced in order to regularize the properties of an otherwise unnormalizable probability distribution.

way of the corrections to Eqs. (3.13), (3.15). Such contributions are essential for analyzing questions pertaining to the behavior *beyond* the bifurcation point, such as the coexistence line between simultaneously stable steady states, metastability, spinodal decomposition, and so forth. In this section we assume that the corrections to the dominant terms can be obtained through the power series

$$\delta = \epsilon^b \delta_1 + \epsilon^{2b}\delta_2 + \cdots, \qquad D = \epsilon^f D_1 + \epsilon^{2f} D_2 + \cdots$$

This looks a priori very restrictive. However, as frequently done in singular perturbation schemes, it will be *imposed* on the equation. If the latter cannot accept solutions of this form, the difficulty will show up by the impossibility of satisfying the appropriate solvability conditions.

Actually, it turns out that the best way of discussing higher order terms is in terms of the cumulant generating function, Eq. (3.7).[23] To preserve continuity, however, we briefly outline here the higher order terms of the perturbation series in the ψ representation adopted in Section 3. On inspecting Eq. (3.3), we see that there are two sources of correction. One arises from additional $\epsilon^a \xi_{\mathbf{r}}$ factors in the coefficients of terms that were retained in the dominant order. Another arises from the factor $\epsilon^a \xi_r^2\, \partial\psi/\partial\xi_r$, which was absent in the dominant order. Remembering that $a = 3/4$ and that in the analysis of Section 3 we had stopped at order $\epsilon^{1/2}$, we see that we may set

$$\psi = \psi^{(0)} + \epsilon^{1/4}\psi^{(1)} + \cdots \tag{4.1}$$

where $\psi^{(0)}$ is given by Eqs. (3.11) and (3.13) and $\psi^{(1)}$ satisfies the equation

$$\sum_{\mathbf{r}} \xi_{\mathbf{r}}\left[\frac{\partial^3\psi^{(1)}}{\partial\xi_{\mathbf{r}}^3} + \delta_1 \frac{\partial\psi^{(1)}}{\partial\xi_{\mathbf{r}}} - \frac{D_1}{2d}\sum_{\boldsymbol{\lambda}}\left(\frac{\partial\psi^{(1)}}{\partial\xi_{\mathbf{r}+\boldsymbol{\lambda}}} - \frac{\partial\psi^{(1)}}{\partial\xi_{\mathbf{r}}}\right)\right] - 4\sum_{\mathbf{r}} \xi_{\mathbf{r}}^2\psi^{(1)}$$
$$= 6\sum_{\mathbf{r}} \xi_{\mathbf{r}}^2 \frac{\partial\psi^{(0)}}{\partial\xi_{\mathbf{r}}} \tag{4.2}$$

As in Section 3, we are looking for symmetric solutions of this equation. One can easily check that this rules out the detailed balance solutions corresponding to deletion of the sum over $\mathbf{r}$ in Eq. (4.2) and to the cancellation of one $\xi_{\mathbf{r}}$ factor. To analyze the full equation (4.2) we again perform a Mellin–Fourier transform, Eq. (3.11). We obtain

$$\sum_{\mathbf{r}} -\frac{\partial}{\partial\theta_{\mathbf{r}}}\left[\theta_{\mathbf{r}}^3 + \delta_1\theta_{\mathbf{r}} - \frac{D_1}{2d}\sum_{\boldsymbol{\lambda}}(\theta_{\mathbf{r}+\boldsymbol{\lambda}} - \theta_{\mathbf{r}})\right]R^{(1)} - 4\sum_{\mathbf{r}}\frac{\partial^2 R^{(1)}}{\partial\theta_{\mathbf{r}}^2}$$
$$= 6\sum_{\mathbf{r}}\frac{\partial^2}{\partial\theta_{\mathbf{r}}^2}\theta_{\mathbf{r}}R^{(0)} \tag{4.3}$$

Setting

$$R^{(1)} = R^{(0)}\Xi \tag{4.4}$$

and performing explicitly the differentiations on the right-hand side of Eq. (4.3), we get the more explicit form

$$\sum_{\mathbf{r}} \left\{ 4 \frac{\partial^2 \Xi}{\partial \theta_{\mathbf{r}}^2} - \left[\theta_{\mathbf{r}}^3 + \delta_1 \theta_{\mathbf{r}} - \frac{D_1}{2d} \sum_{\lambda} (\theta_{\mathbf{r}+\lambda} - \theta_{\mathbf{r}}) \right] \frac{\partial \Xi}{\partial \theta_{\mathbf{r}}} \right\}$$
$$= 3 \sum_{\mathbf{r}} \left\{ \frac{1}{2} \theta_{\mathbf{r}} (3\theta_{\mathbf{r}}^2 + \delta_1 + D_1) + (\theta_{\mathbf{r}}^3 + \delta_1 \theta_{\mathbf{r}}) \right.$$
$$\left. - \frac{1}{8} \theta_{\mathbf{r}} \left[\theta_{\mathbf{r}}^3 + \delta_1 \theta_{\mathbf{r}} - \frac{D_1}{2d} \sum_{\lambda} (\theta_{\mathbf{r}+\lambda} - \theta_{\mathbf{r}}) \right]^2 \right\} \tag{4.5}$$

Since the right-hand side is odd in $\theta_{\mathbf{r}}$, this equation admits odd solutions,

$$\Xi = \sum_{\mathbf{r}} \left(\alpha_{\mathbf{r}} \theta_{\mathbf{r}} + \sum_{\mathbf{r}'\mathbf{r}''} \alpha_{\mathbf{r}\mathbf{r}'\mathbf{r}''} \theta_{\mathbf{r}} \theta_{\mathbf{r}'} \theta_{\mathbf{r}''} + \cdots \right) \tag{4.6}$$

The coefficients $\alpha_{\{\mathbf{r}\}}$ can be computed straightforwardly by inserting into Eq. (4.5) and by identifying equal powers of $\theta_{\mathbf{r}}$. For $\alpha_{\mathbf{r}}$ this gives

$$\alpha_{\mathbf{r}} = -\tfrac{3}{2}(3 + D_1/\delta_1) \tag{4.7}$$

The ratio D_1/δ_1 remains undetermined at this stage. To compute it one should introduce the solvability conditions for Eq. (4.5).

Keeping in mind Eqs. (4.1), (4.4), (4.6), and (4.7) as well as the scaling leading to Eq. (3.15), we obtain

$$\psi^{(1)}/\psi^{(0)} \sim \epsilon^{1/4}\theta_{\mathbf{r}} + \cdots \sim \epsilon^{1/2} k_{\mathbf{r}} + \cdots \qquad \text{with} \quad k_{\mathbf{r}} \simeq O(1)$$

Thus, $\psi^{(1)}$ is indeed a correction to the dominant order. No divergence is possible in our procedure unless $\delta_1 = 0$ accidentally, in which case the calculation must be pushed to the next order.

The correction to the Landau–Ginzburg functional just worked out also shows that the second moment of the probability distribution—including the correlation function—is given correctly by the dominant approximation, Eq. (3.15). The situation may be different for higher moments. A particularly striking example is the third-order variance $\langle \delta X^3 \rangle$, or, in the notation of Section 3, $\langle k_{\mathbf{r}}^3 \rangle$. Within the framework of Section 3, $\langle k_{\mathbf{r}}^3 \rangle = 0$, since $R^{(0)}$ is even in $k_{\mathbf{r}}$. On the other hand, $R^{(1)}$ contains odd terms and gives thus a non-vanishing contribution to $\langle k_{\mathbf{r}}^3 \rangle$. Within the framework of our formalism this quantity—and in fact a whole set of higher moments and correlation functions—can be computed quite straightforwardly. The main point to realize is that $\{\xi_{\mathbf{r}} = 0\}$ is an ordinary point of the differential equation (3.3). Hence, on differentiating successively both sides in $\xi_{\mathbf{r}}$ and then setting $\{\xi_{\mathbf{r}} = 0\}$ one can evaluate $(\partial^3 \psi / \partial \xi_{\mathbf{r}}^3)|_{\{\xi_{\mathbf{r}}=0\}}$, etc. Let us outline the procedure for the third-order variance. We obtain from Eq. (3.3)

$$\left.\frac{\partial^3 \psi}{\partial \xi_{\mathbf{r}}^3}\right|_{\{\xi_{\mathbf{r}}=0\}} + \delta \left.\frac{\partial \psi}{\partial \xi_{\mathbf{r}}}\right|_{\{\xi_{\mathbf{r}}=0\}} - \frac{D}{2d} \sum_{\lambda} \left(\frac{\partial \psi}{\partial \xi_{\mathbf{r}+\lambda}} - \frac{\partial \psi}{\partial \xi_{\mathbf{r}}} \right)_{\{\xi_{\mathbf{r}}=0\}} = 0 \tag{4.8}$$

Now from Eq. (2.8)

$$\left.\frac{\partial \psi}{\partial \xi_{\mathbf{r}}}\right|_{\{\xi_{\mathbf{r}}=0\}} = o(1)$$

Hence, from Eq. (4.8)

$$\left.\frac{\partial^3 \psi}{\partial \xi_{\mathbf{r}}^3}\right|_{\{\xi_{\mathbf{r}}=0\}} = o(1)$$

or, from Eq. (2.6b)

$$\langle(\delta X)^3\rangle = 3\langle(\delta X)^2\rangle - 2\langle X\rangle + o(1) \tag{4.9}$$

We have therefore the explicit expression of the third-order variance in terms of quantities that can be evaluated from the theory presented in Section 3.

We close this section with some comments concerning the approach to the bifurcation point along the nonsymmetric path, $\delta \neq \delta'$. In this case $\bar{x}_{\mathbf{r}} \neq 1$, and one has to use Eq. (2.6a) instead of (2.6b). Then Eq. (2.7) becomes

$$\begin{aligned}\sum_{\mathbf{r}} (1 - S_{\mathbf{r}})S_{\mathbf{r}}^2\Big[\frac{1}{\Delta V^2}\frac{\partial^3\psi}{\partial S_{\mathbf{r}}^3} + \frac{3}{\Delta V}(\bar{x}_{\mathbf{r}} - 1)\frac{\partial^2\psi}{\partial S_{\mathbf{r}}^2} + (3\bar{x}_{\mathbf{r}}^2 - 6\bar{x}_{\mathbf{r}})\frac{\partial\psi}{\partial S_{\mathbf{r}}} \\ + \Delta V(\bar{x}_{\mathbf{r}}^3 - 3\bar{x}_{\mathbf{r}}^2)\psi\Big] \\ + \sum_{\mathbf{r}} (1 - S_{\mathbf{r}})\Big\{(3 + \delta)\frac{\partial\psi}{\partial S_{\mathbf{r}}} + \Delta V[\bar{x}_{\mathbf{r}}(3 + \delta) - (1 + \delta')]\psi\Big\} \\ - \frac{D}{2d}\sum_{\mathbf{r}\lambda}(1 - S_{\mathbf{r}})\left(\frac{\partial\psi}{\partial S_{\mathbf{r}+\lambda}} - \frac{\partial\psi}{\partial S_{\mathbf{r}}}\right) = 0\end{aligned} \tag{4.10}$$

We now consider the case of "weak field" and set

$$\bar{x}_{\mathbf{r}} = 1 + \epsilon^g h \tag{4.11}$$

in addition to Eqs. (3.1), (3.2), (3.4). We thus obtain, instead of Eq. (3.3),

$$\begin{aligned}\sum_{\mathbf{r}} - \xi_{\mathbf{r}}[1 + O(\epsilon^a)]\Big[\epsilon^{2(1-a)}\frac{\partial^3\psi}{\partial\xi_{\mathbf{r}}^3} + 3\epsilon^{1-a+g}h\frac{\partial^2\psi}{\partial\xi_{\mathbf{r}}^2} + (3\epsilon^{2g}h^2 + \delta_1\epsilon^b)\frac{\partial\psi}{\partial\xi_{\mathbf{r}}}\Big] \\ + \sum_{\mathbf{r}} - \xi_{\mathbf{r}}[2\epsilon^a\xi_{\mathbf{r}} + O(\epsilon^{2a})]\Big[3\left(-1 + \epsilon^{2g}h^2\frac{\partial\psi}{\partial\xi_{\mathbf{r}}}\right) \\ - (2\epsilon^{-1+a} + 3\epsilon^g h)\psi\Big] + \frac{D_1}{2d}\sum_{\mathbf{r}\lambda}\epsilon^f\xi_{\mathbf{r}}\left(\frac{\partial\psi}{\partial\xi_{\mathbf{r}+\lambda}} - \frac{\partial\psi}{\partial\xi_{\mathbf{r}}}\right) = 0\end{aligned} \tag{4.12}$$

The dominant part of this equation can be analyzed as in Section 3. Setting $a = \frac{3}{4}$, $b = f = \frac{1}{2}$, and $g = \frac{1}{4}$ and adopting the detailed balance solution, we obtain

$$\frac{\partial^3\psi^{(0)}}{\partial\xi_{\mathbf{r}}^3} + 3h\frac{\partial^2\psi^{(0)}}{\partial\xi_{\mathbf{r}}^2} + (\delta_1 + 3h^2)\frac{\partial\psi^{(0)}}{\partial\xi_{\mathbf{r}}} - \frac{D_i}{2d}\sum_{\boldsymbol{\lambda}}\left(\frac{\partial\psi^{(0)}}{\partial\xi_{\mathbf{r}\lambda}} - \frac{\partial\psi^{(0)}}{\partial\xi_{\mathbf{r}}}\right) = 4\xi_{\mathbf{r}}\psi^{(0)} \tag{4.13}$$

We see that the difference between this relation and Eq. (3.10) describing the symmetric bifurcation case is the presence of a second derivative term and the modification of the coefficient of the first derivative term.

Equation (4.13) can again be solved by performing a Mellin–Fourier transform. We obtain in this way

$$R_{h\neq 0}^{(0)} \propto \exp\left\{-\frac{1}{4}\sum_{\mathbf{r}}\left[(\partial_1 + 3h^2)\frac{\theta_{\mathbf{r}}^2}{2} + h\theta_{\mathbf{r}}^3 + \frac{\theta_{\mathbf{r}}^4}{4} + \frac{D_1}{8d}\sum_{\boldsymbol{\lambda}}(\theta_{\mathbf{r}+\lambda} - \theta_{\mathbf{r}})^2\right]^4\right\} \tag{4.14}$$

Note the presence of the cubic term in the exponential. Such terms are known to arise in the theory of critical phenomena when an external field is present, or when the system has already entered the condensed phase.[19]

5. SYSTEM WITH QUADRATIC NONLINEARITIES. THE ABSORBING STATE CASE

In this section we briefly examine the stochastic aspects of bifurcation phenomena in systems involving one concentration variable and a quadratic rate law. A good illustration is a bimolecular model due again to Schlögl[17]:

$$\begin{aligned} \mathrm{A} + \mathrm{X} &\underset{k_2}{\overset{k_1}{\rightleftarrows}} 2\mathrm{X} \\ \mathrm{B} + \mathrm{X} &\underset{k_4}{\overset{k_3}{\rightleftarrows}} \mathrm{C} \end{aligned} \tag{5.1}$$

where A, B, C are controlled from outside. Setting

$$\begin{aligned} k_3B/k_2 &= \beta\,\Delta V \\ k_1A/k_2 &= (\beta + \delta)\,\Delta V \\ k_4C/k_2 &= c\,\Delta V, \qquad \bar{x} = \bar{X}/\Delta V, \qquad \tau = k_2t \end{aligned} \tag{5.2}$$

we obtain the phenomenological rate equation

$$d\bar{x}/d\tau = -\bar{x}^2 + \delta\bar{x} + c \tag{5.3}$$

whose only physically acceptable steady-state solution is

$$\bar{x} = [\delta + (\delta^2 + 4c)^{1/2}]/2 \qquad \text{for} \quad c \neq 0 \tag{5.4a}$$

On the other hand, if $c = 0$ but $\delta \geqslant 0$ we have two solutions:

$$\begin{aligned} \bar{x}_0 &= 0 \qquad \text{(unstable)} \\ \bar{x}_+ &= \delta \qquad \text{(stable)} \end{aligned} \tag{5.4b}$$

$\delta = 0$ is therefore a bifurcation point.

In the generating function representation, the multivariate master equation at the steady state reads

$$\sum_{\mathbf{r}} (1 - S_{\mathbf{r}})\left\{S_{\mathbf{r}} \frac{1}{\Delta V} \frac{\partial^2 F}{\partial S_{\mathbf{r}}^2} + [(\beta + \delta)(1 - S_{\mathbf{r}}) - \delta] \frac{\partial F}{\partial S_{\mathbf{r}}} - c\,\Delta V F\right\}$$
$$+ \frac{D}{2d} \sum_{\mathbf{r}} (S_{\mathbf{r}} - 1) \sum_{\boldsymbol{\lambda}} \left(\frac{\partial F}{\partial S_{\mathbf{r}+\boldsymbol{\lambda}}} - \frac{\partial F}{\partial S_{\mathbf{r}}}\right) = 0 \tag{5.5}$$

Introducing, as in Section 3, the scaling

$$\epsilon = 1/\Delta V \ll 1, \qquad S_{\mathbf{r}} = 1 + \epsilon^a \xi_{\mathbf{r}}, \quad 0 < a < 1 \tag{5.6a}$$

as well as the auxiliary function ψ, through

$$F = \psi \prod_{\mathbf{r}} \exp[\Delta V \bar{x}(S_{\mathbf{r}} - 1)] \tag{5.6b}$$

we obtain the detailed balance solution:

$$(1 + \epsilon^a \xi_{\mathbf{r}})\epsilon^{1-a} \frac{\partial^2 \psi}{\partial \xi_{\mathbf{r}}^2} + [2\bar{x} - \delta + \epsilon^a(2\bar{x} - \beta - \delta)\,\xi_{\mathbf{r}}] \frac{\partial \psi}{b \xi_{\mathbf{r}}}$$
$$- \epsilon^{2a-1}(\beta\bar{x} - c)\xi_{\mathbf{r}}\psi - \frac{D}{2d} \sum_{\boldsymbol{\lambda}} \left(\frac{\partial \psi}{\partial \xi_{\mathbf{r}+\boldsymbol{\lambda}}} - \frac{\partial \psi}{\partial \xi_{\mathbf{r}}}\right) = 0 \tag{5.7}$$

Two cases can now be envisaged.

5.1. $c \neq 0$

For this case $\bar{x} \neq 0$. For $0 < a < 1$ [see Eq. (3.2)], one has a nontrivial solution for $a = \frac{1}{2}$, in which case

$$(2\bar{x} - \delta) \frac{\partial \psi^{(0)}}{\partial \xi_{\mathbf{r}}} - (\beta\bar{x} - c)\xi_{\mathbf{r}}\psi^{(0)} - \frac{D}{2d} \sum_{\boldsymbol{\lambda}} \left(\frac{\partial \psi^{(0)}}{\partial \xi_{\mathbf{r}+\boldsymbol{\lambda}}} - \frac{\partial \psi^{(0)}}{\partial \xi_{\mathbf{r}}}\right) = 0 \tag{5.8}$$

Performing a Mellin–Fourier transform, Eq. (3.11), we easily get

$$R^{(0)} \propto \exp\left\{-\frac{1}{\beta\bar{x} - c} \sum_{\mathbf{r}} \left[\frac{2\bar{x} - \delta}{2} \theta_{\mathbf{r}}^2 + \frac{D}{8d} \sum_{\boldsymbol{\lambda}} (\theta_{\mathbf{r}+\boldsymbol{\lambda}} - \theta_{\mathbf{r}})^2\right]\right\} \tag{5.9}$$

We find therefore a multi-Gaussian distribution. This is natural, since for $c \neq 0$ the system does not undergo bifurcation.

5.2. $c = 0$

In this case $\bar{x}_+ = \delta$ and $\bar{x}_0 = 0$. Looking first at Eq. (5.5), we see that the term in F is absent. Hence this equation admits the exact, properly normalized solution

$$F = 1 \tag{5.10}$$

This reflects the existence of an absorbing state $\bar{x}_0 = 0$ in the system. For any $\epsilon > 0$ one would expect uniqueness of solutions, and hence (5.10) should be the only solution. What happens in the thermodynamic limit $\epsilon \to 0$? Let us analyze this question by "forcing" the system to admit a solution centered on $\bar{x}_+$ for all $\delta > 0$ as $\delta \to 0$. To follow this latter limit we also set

$$\delta = \epsilon^b \delta_1 + \cdots, \qquad D = \epsilon^f D_1 + \cdots \tag{5.11}$$

The dominant terms of Eq. (5.7) are then contained in the expression

$$\epsilon^{1-a} \frac{\partial^2 \psi}{\partial \xi_{\mathbf{r}}{}^2} + (\delta_1 \epsilon^b - \epsilon^a \beta \xi_{\mathbf{r}}) \frac{\partial \psi}{\partial \xi_{\mathbf{r}}} - \epsilon^{2a-1+b} \beta \delta_1 \xi_{\mathbf{r}} \psi$$
$$- \frac{D_1}{2d} \epsilon^f \sum_{\boldsymbol{\lambda}} \left(\frac{\partial \psi}{\partial \xi_{\mathbf{r}+\boldsymbol{\lambda}}} - \frac{\partial \psi}{\partial \xi_{\mathbf{r}}} \right) = 0 \tag{5.12}$$

The behavior of the solutions of this equation crucially depends upon the way in which ϵ^b goes to zero relative to ϵ^a, that is, ultimately, on the distance from the bifurcation point. Thus, we distinguish three subcases:

(i) $b < a$. The situation is then identical to the case of Section 5.1, and is described by the Gaussian approximation.

(ii) $b = a$. For $b = a = f = \frac{1}{2}$ all terms in (5.12) are of the same order. Switching to Mellin–Fourier space, we obtain

$$(\theta_{\mathbf{r}}{}^2 + \delta_1 \theta_{\mathbf{r}} + \beta) R^{(0)} + \beta(\theta_{\mathbf{r}} + \delta_1) \frac{\partial R^{(0)}}{\partial \theta_{\mathbf{r}}} - \frac{D_1}{2d} \sum_{\boldsymbol{\lambda}} (\theta_{\mathbf{r}+\boldsymbol{\lambda}} - \theta_{\mathbf{r}}) R^{(0)} = 0 \tag{5.13}$$

Setting

$$\ln R^{(0)} = -\frac{1}{2\beta} \sum_{\mathbf{r}} \theta_{\mathbf{r}}{}^2 - \sum_{\mathbf{r}} \ln(\theta_{\mathbf{r}} + \delta_1) + \Xi$$

we obtain

$$\beta(\theta_{\mathbf{r}} + \delta_1) \frac{\partial \Xi}{\partial \theta_{\mathbf{r}}} = \frac{D_1}{2d} \sum_{\boldsymbol{\lambda}} (\theta_{\mathbf{r}+\boldsymbol{\lambda}} - \theta_{\mathbf{r}})$$

Now, one can easily check that this set of equations is self-contradictory. Indeed, evaluating the mixed derivatives of Ξ, we get

$$\frac{\partial^2 \Xi / \partial \theta_{\mathbf{r}+\boldsymbol{\lambda}} \, \partial \theta_{\mathbf{r}}}{\partial^2 \Xi / \partial \theta_{\mathbf{r}} \, \partial \theta_{\mathbf{r}+\boldsymbol{\lambda}}} = \frac{\theta_{\mathbf{r}+\boldsymbol{\lambda}} + \delta_1}{\theta_{\mathbf{r}} + \delta_1} \neq 1 \tag{5.14}$$

We conclude therefore that subcase (ii) has to be dismissed, at least within the framework of detailed balanced solutions.

(iii) $b > a$. This means that we are very close to the bifurcation point. In Eq. (5.12) the term $\delta_1 \epsilon^b$ can then be neglected. If $a \geqslant \frac{1}{2}$, one obtains, to zeroth order in the perturbation expansion, the properly normalized solution

$\psi = 1$. This reflects the existence of the absorbing boundary, as pointed out earlier in this subsection. For $a < \frac{1}{2}$ one may have a nonconstant solution for $a = f = b = 1 - a$:

$$-\beta\xi_{\mathbf{r}} \frac{\partial\psi^{(0)}}{\partial\xi_{\mathbf{r}}} - \beta\delta_1\xi_{\mathbf{r}}\psi^{(0)} - \frac{D_1}{2d}\sum_{\lambda}\left(\frac{\partial\psi^{(0)}}{\partial\xi_{\mathbf{r}+\lambda}} - \frac{\partial\psi^{(0)}}{\partial\xi_{\mathbf{r}}}\right) = 0 \quad (5.15)$$

Switching to Mellin–Fourier space, we obtain

$$\beta R^{(0)} + \beta(\theta_{\mathbf{r}} + \delta_1)\frac{\partial R^{(0)}}{\partial\theta_{\mathbf{r}}} - \frac{D_1}{2d}\sum_{\lambda}(\theta_{\mathbf{r}\lambda} - \theta_{\mathbf{r}})R^{(0)} = 0$$

As in subcase (ii), we seek for a solution of the form

$$\ln R^{(0)} = -\sum_{\mathbf{r}}\ln(\theta_{\mathbf{r}} + \delta_1) + \Xi$$

in which case Ξ satisfies the relation

$$\beta(\theta_{\mathbf{r}} + \delta_1)\frac{\partial\Xi}{\partial\theta_{\mathbf{r}}} = -\frac{D_1}{2d}\sum_{\lambda}(\theta_{\mathbf{r}+\lambda} - \theta_{\mathbf{r}})$$

As explained above, this system of equations is self-contradictory. We therefore reach the conclusion that sufficiently close to the bifurcation point, the system *cannot* admit a detailed balance steady-state solution around the nontrivial state $\bar{x}_+$. Thus, the absorbing state $F = 1$ [cf. Eq. (5.10)] remains the only acceptable solution. In other words, any sort of critical behavior related to the approach to the bifurcation point is to be ruled out. A similar conclusion has been reached in the renormalization group analysis by Dewel *et al.*[13]

6. CONCLUDING REMARKS

In this paper we determined the conditions under which a jump process characteristic of the behavior of a reaction–diffusion system reduces, *in the vicinity of a bifurcation point*, to a description in terms of the Landau–Ginzburg functional familiar from renormalization group analysis of phase transitions. Our derivation shows that this reduction is by no means automatic. Rather, it appears to require an asymptotic element (ΔV large, δ small) as well as appropriate types of nonlinearities. In particular, for a quadratic nonlinearity involving an absorbing state we arrived at the conclusion that sufficiently close to the bifurcation point the system was unable to show critical behavior.

We believe that the perturbative method we set up could prove useful for other purposes as well. In Section 4 we outlined briefly some applications related to higher order approximations. Two further problems, which remain largely unexplored because of considerable technical difficulties, can also be considered within our formalism. One is time-dependent behavior, in connection with the evolution from an initial state close to an unstable solution into a final stable steady state.[24,25] The other is symmetry-breaking bifurcations.[14] In the latter, of course, additional difficulties are to be expected, arising from the presence of at least two coupled concentration variables.

In much of our analysis, we were led to consider steady-state solutions of the detailed balance type. A glance at the general multivariate master equation [Eq. (1.2), (2.5), or (5.5)] suffices to convince oneself that in the presence of diffusion such solutions should not necessarily exist in the most general case. Already in Section 5 we were led to contradictions after assuming their validity. This is natural after all: since the different spatial cells are coupled by diffusion, there is a flow of probability between them which tends to compromise the cancellation between "forward" and "backward" processes in each individual cell.

Our analysis sheds some light on this question by showing that the passage to detailed balance solutions is accompanied by the existence of an *asymptotic element* ($\epsilon \ll 1$, $\delta \ll 1$) in the problem. In a way, because ΔV can be taken large for δ small, the spatial cells are loosely coupled through all degrees of freedom *except* the ones that undergo bifurcation (the *order parameter*; see also comments by Graham[26].) Thus, the problem reduces effectively to one involving long-range fluctuations of a single degree of freedom. The latter remain of course coupled, but their coupling keeps no track of the initial partition of the system into small spatial cells.

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