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Statistical Physics of Bifurcation, Spatial Structures, and Fluctuations of Chemical Reactions

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Abstract. We present a fully nonlinear stochastic theory of chemical reactions closely below, at and above instability points. As explicit example we treat the Prigogine-Lefever-Nicolis model of two interacting kinds of molecules, generalizing it to two and three dimensions, to a mode continuum, and taking into account fluctuations. Adopting a description by means of birth and death processes we establish the master-equation, and proceed to the Fokker-Planck equation. This is transformed to new coordinates connected with unstable and stable modes. After adiabatic elimination of the stable modes, we obtain a functional Fokker-Planck equation for a continuous set of "unstable" modes. This final equation can now be treated by standard methods. In one dimension our results reveal striking analogies to the Ginzburg-Landau theory of superconductivity, to the continuous mode laser and to small-band excitations at hydrodynamical instabilities, while in three dimensions, in thin layers a hexagonal structure similar to Bénard cells occurs.

§ 1. Introduction

Physicists have studied the thermodynamics and statistics of chemical reactions since a long time. More recently, new types of chemical reactions have been investigated both experimentally and theoretically [1–22]. These chemical reactions occur far from thermal equilibrium and are accompanied by spatial and/or temporal oscillations. To account for these new patterns ("dissipative structures" [15]) several reaction-diffusion models have been proposed which use nonlinear kinetic equations for the numbers (or concentrations) of reacting molecules. The spatial and temporal behaviour of the concentrations of the molecules under consideration is controlled by external parameters, e.g. by the concentration of other reactants which are fed into the reactor. If e.g. the concentration b of a "controlling" reactant is smaller than a certain critical value b_c, the system is structureless. At the "threshold" $b=b_c$ this configuration becomes unstable and finally for $b>b_c$, completely new types of solutions to the kinetic equations occur. The old solution "bifurcates" into the new ones. This bifurcation is accompanied by a gain of information. Due to the nonlinearity of the kinetic equations, the physical nature of these transitions was not completely clear, however. An impetus to a reconsideration of this problem came from a seemingly quite different discipline, namely laser physics. Here it could be shown in all details that the laser threshold can be interpreted as a non-equilibrium phasetransition having profound analogies to phase transitions of systems in thermal equilibrium [23–30]. This has lead to a discussion of chemical reaction models which exhibit a similar phase transition-like behaviour [18–21]. In these models a *single kind* of molecules is treated explicitly. The mathematical structure of the models which take into account fluctuations is very similar to that of models of tunnel diodes [31]. Prigogine, Lefever and Nicolis [15–17] and others dealt with *two kinds* of

molecules. As has been shown this model describes the occurrence of spatial and temporal patterns. Recently Tomita *et al.* [32] treated temporal oscillations using some kind of linearization method which takes into account fluctuations but which has to exclude the immediate transition region where the instability occurs. On the other hand Nicolis [17] and other authors [33] neglected the fluctuations and applied bifurcation theory [34] to treat the branching of the new solutions. There is some intrinsic difficulty with the neglect of fluctuations, however, because it is well known from phase transition theory and from the explicit example of the laser that just at the transition point fluctuations play a major role.

In our paper we give a novel approach to the bifurcation problem which includes fluctuations and thus seems promising to replace the hitherto used bifurcation theory. As an explicit example we treat the Prigogine-Lefever-Nicolis model [15–17], which we incidentally generalize to two and three dimensions, and to a mode continuum. We present the results for the socalled soft mode instability whereas in a subsequent paper essentially the same method will be applied to instabilities with temporal oscillations. The main results of our analysis (including the hitherto known results of stability considerations) can be summarized as follows:

For $b<b_c$, the equilibrium concentrations $M(\mathbf{x})$, $N(\mathbf{x})$ of the two types of molecules X, Y at space point $\mathbf{x}$, are constant

$$\mathbf{M}(\mathbf{x})=M_0(\mathbf{x})\equiv a, \qquad N(\mathbf{x})=N_0(\mathbf{x})\equiv b/a.$$

At $b=b_c$ waves of the form $\xi_{\mathbf{k}}\chi_{\mathbf{k}}(\mathbf{x})$ (where e.g. $\chi\propto \sin \mathbf{k}\,\mathbf{x}$) and $|k|=k_c$ become unstable.

For $b\gtrless b_c$ we decompose $M(\mathbf{x})$, $N(\mathbf{x})$ into

$$M(\mathbf{x})=a+q_1(\mathbf{x}); \qquad N(\mathbf{x})=b/a+q_2(\mathbf{x}). \tag{1.1}$$

The (large) deviations $q_j(\mathbf{x})$ are represented as superpositions

$$q_j(\mathbf{x})=\sum_{\mathbf{k}}\left(O_j^{(1)}\,\xi_{\mathbf{k}}(\mathbf{x})+O_j^{(2)}\,\eta_{\mathbf{k}}(\mathbf{x})\right)\chi_{\mathbf{k}}(\mathbf{x}), \tag{1.2}$$

where $\xi_{\mathbf{k}}$ and $\eta_{\mathbf{k}}$ are treated as slowly varying amplitudes and O are certain operators defined below.

We eliminate the damped modes adiabatically and find for $\xi_k(\mathbf{x})$, $|\mathbf{k}|=k_c$, the following Fokker-Planck equation:

a) in one dimension:

$$\begin{aligned}\dot f=&\Big[-\int dx\,(\delta/\delta\xi(x))\big((\lambda_0+\lambda^{(1)}\nabla^2)\xi(x)-A\xi^3(x)\big)\\&+\int d^3x G_{11}\delta^2/\delta\xi^2\Big]f\end{aligned} \tag{1.3}$$

(where ξ is assumed real. For complex ξ see 1.4).

The stationary solution of it is the well-known Ginzburg-Landau functional of the theory of superconductivity and of the continuous mode laser [23]. This allows us to interpret the present chemical instability as a quasi-phase transition including symmetry breaking (bifurcation).

b) in three dimensions:

$$\begin{aligned}\dot f=&\Big[-\int d^3x\sum_{\mathbf{k}}\big[(\delta/\delta\xi_{\mathbf{k}}(\mathbf{x}))\big((\lambda_0+\lambda^{(1)}\nabla^2)\xi_{\mathbf{k}}(\mathbf{x})\\&+\sum_{\mathbf{k}'\mathbf{k}''}\bar c_1 I_{\mathbf{k}\mathbf{k}'\mathbf{k}''}\xi_{\mathbf{k}'}(\mathbf{x})\xi_{\mathbf{k}''}(\mathbf{x})\\&-\sum_{\mathbf{k}'\mathbf{k}''\mathbf{k}'''}\bar a_1 J_{\mathbf{k}\mathbf{k}'\mathbf{k}''\mathbf{k}'''}\xi_{\mathbf{k}'}(\mathbf{x})\xi_{\mathbf{k}''}(\mathbf{x})\xi_{\mathbf{k}'''}(\mathbf{x})\big)\\&-G_{11}\delta^2/\big(\delta\xi_{\mathbf{k}}(x)\delta\xi^*_{\mathbf{k}}(\mathbf{x})\big)\big]f; \qquad \xi_{\mathbf{k}}=\xi^*_{-\mathbf{k}}.\end{aligned} \tag{1.4}$$

The coefficients λ_0, $\lambda^{(1)}$, $\bar c_1$, $\bar a_1$, I, J and G are explicitly given in the following. Here we just mention that in a thin layer, the solutions of (1.4) are identical to those of hexagonal Bénard cells or rolls in hydrodynamics [30, 36].

These close analogies to the Ginzburg-Landau theory of superconductivity, to the theory of laser fluctuations and to hydrodynamic instabilities are a further contribution to our assertion [30, 37, 38] that there are large classes of phenomena in physics, chemistry and other sciences which exhibit striking similarities at the transition from disorder to order.

§ 2. Master Equation and Fokker-Planck Equation

We consider the following reaction scheme [15–17]

$$\begin{aligned}A&\to X\\B+X&\to Y+D\\2X+Y&\to 3X\\X&\to E\end{aligned} \tag{2.1}$$

where the concentrations of the molecules of kind A, B are externally given and kept fixed, while the numbers of molecules of kind X and Y are assumed to be variable. They are denoted by M, N respectively. Because we want to take into account spatial effects, we divide the space in which the chemical reaction takes place into cells which still contain a large number of molecules (compared to unity). We distinguish the cells by an index $\mathbf{l}$ and denote the number of molecules in cell $\mathbf{l}$ by $M_{\mathbf{l}}$, $N_{\mathbf{l}}$. We introduce as usual suitable dimensionless constants a, b which are proportional to the concentrations of the molecules of kind A, B. We obtain the following master equation for the probability distribution $P(\ldots, M_{\mathbf{l}}; N_{\mathbf{l}}; \ldots)$ which gives us the joint probability to find $M_{\mathbf{l}'}, N_{\mathbf{l}'}, \ldots, M_{\mathbf{l}}, N_{\mathbf{l}}, \ldots$

molecules in cells $\mathbf{l}', \ldots, \mathbf{l}$, [39]

$$\begin{aligned}\dot{P}(\ldots; M_{\mathbf{l}}, N_{\mathbf{l}}; \ldots) &= \sum_{\mathbf{l}} v\big[a P(\ldots; M_{\mathbf{l}}-1, N_{\mathbf{l}}; \ldots)\\ &+ b(M_{\mathbf{l}}+1)v^{-1} P(\ldots; M_{\mathbf{l}}+1, N_{\mathbf{l}}-1; \ldots)\\ &+ (M_{\mathbf{l}}-2)(M_{\mathbf{l}}-1)(N_{\mathbf{l}}+1)v^{-3}\\ &\cdot P(\ldots; M_{\mathbf{l}}-1, N_{\mathbf{l}}+1; \ldots)\\ &+ (M_{\mathbf{l}}+1)v^{-1} P(\ldots; M_{\mathbf{l}}+1, N_{\mathbf{l}}; \ldots)\\ &- P(\ldots; M_{\mathbf{l}}, N_{\mathbf{l}}; \ldots)\big(a+(b+1)M_{\mathbf{l}}v^{-1}\\ &+ M_{\mathbf{l}}(M_{\mathbf{l}}-1)N_{\mathbf{l}}v^{-3}\big) + \sum_{\mathbf{l},\mathbf{a}} \big[D_1'\{(M_{\mathbf{l}+\mathbf{a}}+1)\\ &\cdot P(\ldots; M_{\mathbf{l}}-1, N_{\mathbf{l}}; \ldots; M_{\mathbf{l}+\mathbf{a}}+1, N_{\mathbf{l}+\mathbf{a}}; \ldots)\\ &- M_{\mathbf{l}+\mathbf{a}} P(\ldots; M_{\mathbf{l}}, N_{\mathbf{l}}; \ldots; M_{\mathbf{l}+\mathbf{a}}, N_{\mathbf{l}+\mathbf{a}}; \ldots)\}\\ &+ D_2'\{(N_{\mathbf{l}+\mathbf{a}}+1)\\ &\cdot P(\ldots; M_{\mathbf{l}}, N_{\mathbf{l}}-1; \ldots; M_{\mathbf{l}+\mathbf{a}}, N_{\mathbf{l}+\mathbf{a}}+1; \ldots)\\ &- N_{\mathbf{l}} P(\ldots; M_{\mathbf{l}}, N_{\mathbf{l}}; \ldots; M_{\mathbf{l}+\mathbf{a}}, N_{\mathbf{l}+\mathbf{a}}; \ldots)\}\big].\end{aligned} \tag{2.2}$$

In it v is the volume of a cell, $\mathbf{l}$. The first sum takes into account the chemical reactions, the second sum containing the "diffusion constants" D_1', D_2' takes into account the diffusion of the two kinds of molecules. The sum over $\mathbf{a}$ runs over the nearest neighbouring cells of the cell $\mathbf{l}$. If the numbers $M_{\mathbf{l}}$, $N_{\mathbf{l}}$ are sufficiently large compared to unity and if the function P is slowly varying with respect to its arguments we may proceed to the Fokker-Planck equation. A detailed analysis which will be published elsewhere shows that van Kampen's objection [40] against the transformation of a master equation into a Fokker-Planck equation does not hold in the present case within a well defined region. This implies in particular $a \gg 1$ and $\mu = (D_1/D_2)^{1/2} < 1$.

To obtain the Fokker-Planck equation we expand expressions of the type $(M_{\mathbf{l}}+1)P(\ldots, M_{\mathbf{l}}+1, N_{\mathbf{l}}, \ldots)$ etc. into a power series with respect to "1" keeping as usual the first three terms. Furthermore we let $\mathbf{l}$ become a continuous index which may be interpreted as the space coordinate $\mathbf{x}$. This requires that we replace the usual derivative by the variational derivative. Incidentically, we replace $M_{\mathbf{l}}/v$, $N_{\mathbf{l}}/v$ by the densities $M(\mathbf{x})$, $N(\mathbf{x})$, and $P(\ldots, M_{\mathbf{l}}, N_{\mathbf{l}}, \ldots)$ by $F(\ldots, M(\mathbf{x}), N(\mathbf{x}), \ldots)$. Since the detailed mathematics of this procedure is well known [41] and does not contribute to the understanding of the physics we just quote the final result

$$\begin{aligned}\dot{F} &= \int d^3x\big[-\{(a-(b+1)M+M^2N+D_1\cdot\nabla^2 M)F\}_{M(\mathbf{x})}\\ &- \{(bM-M^2N+D_2\cdot\nabla^2 N)F\}_{N(\mathbf{x})}\\ &+ \frac{1}{2}\{(a+(b+1)M+M^2N)F\}_{M(\mathbf{x}),M(\mathbf{x})}\\ &- \{(bM+M^2N)F\}_{M(\mathbf{x}),N(\mathbf{x})}\\ &+ \frac{1}{2}\{(bM+M^2N)F\}_{N(\mathbf{x}),N(\mathbf{x})}\\ &+ D_1\big(\nabla(\delta/\delta M(\mathbf{x}))\big)^2(MF) + D_2\big(\nabla(\delta/\delta N(\mathbf{x}))\big)^2(NF)\big].\end{aligned} \tag{2.3}$$

The indices $M(\mathbf{x})$ or $N(\mathbf{x})$ indicate the variational derivative with respect to $M(\mathbf{x})$ or $N(\mathbf{x})$. D_1 and D_2 are the usual diffusion constants. The Fokker-Planck equation (2.3) is still far too complicated to allow for an explicit solution. We therefore proceed in several steps: We first use the known results of the stability analysis of the corresponding rate equations without fluctuations [17]. According to these considerations there exist stable spatially homogeneous and time independent solutions $M(\mathbf{x}) = a$, $N(\mathbf{x}) = b/a$ provided $b < b_c$. We therefore introduce new variables $q_j(\mathbf{x})$ by

$$M(\mathbf{x}) = a + q_1(\mathbf{x}), \qquad N(\mathbf{x}) = b/a + q_2(\mathbf{x}),$$

and obtain the following Fokker-Planck equation:

$$\begin{aligned}\dot{F} &= \int dx\big[-\{((b-1)q_1 + a^2 q_2 + g(q_1,q_2) + D_1\nabla^2 q_1)F\}_{q_1(\mathbf{x})}\\ &- \{(-bq_1 - a^2 q_2 - g(q_1,q_2) + D_2\nabla^2 q_2)F\}_{q_2(\mathbf{x})}\\ &+ \frac{1}{2}\{\hat{D}_{11}(q)F\}_{q_1(\mathbf{x}),q_1(\mathbf{x})} - \{\hat{D}_{12}(q)F\}_{q_1(\mathbf{x}),q_2(\mathbf{x})}\\ &+ \frac{1}{2}\{\hat{D}_{22}(q)F\}_{q_2(\mathbf{x}),q_2(\mathbf{x})}\\ &+ D_1\big(\nabla(\delta/\delta q_1(\mathbf{x}))\big)^2(a+q_1)F\\ &+ D_2\big(\nabla(\delta/\delta q_2(\mathbf{x}))\big)^2(b/a+q_2)F\big].\end{aligned} \tag{2.4}$$

F is now a functional of the variables $q_j(\mathbf{x})$. We have used the following abbreviations

$$g(q_1,q_2) = 2aq_1q_2 + bq_1^2/a + q_1^2 q_2, \tag{2.5}$$

$$\hat{D}_{11} = 2a + 2ab + (3b+1)q_1 + a^2 q_2 + 2aq_1q_2 + (b/a)q_1^2 + q_1^2 q_2, \tag{2.6}$$

$$\hat{D}_{12} = \hat{D}_{22} = 2ab + 3bq_1 + bq_1^2/a + a^2 q_2 + 2aq_1q_2 + q_1^2 q_2. \tag{2.7}$$

§3. Transformation of the Fokker-Planck Equation to Eigensolutions of Linearized Rate Equations

Our further procedure is suggested by considering the rate equations of q_1, q_2. They are obtained from the Fokker-Planck equation (2.4) as the equations of motion of the average values $\overline{q_j} = \int q_j F(Dq)$, where (Dq) denotes functional integration. Keeping in these equations only terms linear in q_1, q_2 we obtain

$$\dot{\mathbf{q}} = K_0\mathbf{q}, \qquad \mathbf{q} = \begin{pmatrix} q_1 \\ q_2 \end{pmatrix}, \tag{3.1}$$

with

$$K_0 = \begin{pmatrix} b-1+D_1\nabla^2 & a^2 \\ -b & -a^2+D_2\nabla^2 \end{pmatrix} \equiv \begin{pmatrix} \mathbf{K}_1 \\ \mathbf{K}_2 \end{pmatrix}. \tag{3.2}$$

By means of the hypothesis

$$\mathbf{q} = e^{\lambda_j t}\mathbf{u}_j \tag{3.3}$$

we obtain

$$K_0\mathbf{u}^j = \lambda_j\mathbf{u}^j. \tag{3.4}$$

If $\lambda_j<0$ the solution is still stable. It is well known, however, that new types of solutions occur if one or several λ_j's become positive. The eigenvalues of (3.4) are given by

$$\lambda_j=\alpha/2\pm(1/2)\sqrt{\alpha^2-4\beta},\quad j=1,2\,(\equiv+,-\sqrt{\ }) \tag{3.5}$$

with

$$\alpha=\left(b-1+(D_1+D_2)\nabla^2-a^2\right) \tag{3.6}$$

and

$$\beta=(1-D_1\nabla^2)(a^2-D_2\nabla^2)+bD_2\nabla^2. \tag{3.7}$$

In our present paper we confine ourselves to the case of real λ's. Because K_0 is, at least in general, not selfadjoint we consider also the solutions of the adjoint equation

$$\bar{\mathbf{u}}^{(j)}K_0=\lambda_j\bar{\mathbf{u}}^{(j)}. \tag{3.8}$$

Note that (3.2), (3.5) and (3.8) still contain the Laplace operator. We now introduce functions $\chi_{\mathbf{k}}(\mathbf{x})$ which fulfill the wave equation in one, two or three dimensions

$$\nabla^2\chi_{\mathbf{k}}(\mathbf{x})=-k^2\chi_{\mathbf{k}}(\mathbf{x}), \tag{3.9}$$

and which will be fixed later by the boundary conditions. We then put

$$\mathbf{u}^{(j,\mathbf{k})}=\begin{pmatrix}O_1^{(j)}\\ O_2^{(j)}\end{pmatrix}\chi_{\mathbf{k}}(\mathbf{x}), \tag{3.10}$$

where $O_i^{(j)}$ are differential operators acting on χ. Similarly we introduce

$$\bar{\mathbf{u}}^{(j,\mathbf{k})}=\chi_{\mathbf{k}}^*(\mathbf{x})\begin{pmatrix}\bar{O}_1^{(j)}\\ \bar{O}_2^{(j)}\end{pmatrix}, \tag{3.11}$$

where the differential operators $\bar{O}$ act to the left hand side, or, if an integration is performed, act on the function standing on the right hand side. We require that u, $\bar{u}$ form an orthonormal set

$$\langle\bar{\mathbf{u}}^{(j,\mathbf{k})},\mathbf{u}^{(j',\mathbf{k}')}\rangle=\delta_{jj'}\delta_{\mathbf{k}\mathbf{k}'} \tag{3.12}$$

where $\langle\cdots\rangle$ denotes the scalar product and integration over d^3x. The O's must be chosen in such a way that (3.10) and (3.11) fulfill the Eqs. (3.4) and (3.8), respectively, and that the orthonormality condition (3.12) is fulfilled. Then the O's take the following general form

$$\begin{aligned}&O_1^{(j)}=b^{-1}(a^2+\lambda_j-D_2\nabla^2)\\ &O_2^{(j)}=1\\ &\bar{O}_1^{(j)}=b(\alpha-2\lambda_j)^{-1}\\ &\bar{O}_2^{(j)}=(b-1+D_1\nabla^2-\lambda_j)\cdot(\alpha-2\lambda_j)^{-1}.\end{aligned} \tag{3.13}$$

Note that there is still one constant arbitrary which we have chosen so to put $O_2=1$. By a transformation which we exhibit by means of the u's

$$\begin{aligned}&u_1^{(j)}=-b^{-1}(a^2+\lambda_j-D_2\nabla^2)\chi\cdot s_j\\ &u_2^{(j)}=\chi\cdot s_j\\ &\bar{u}_1^{(j)}=b(\alpha-2\lambda_j)^{-1}\chi\cdot s_j^{-1}\\ &\bar{u}_2^{(j)}=(b-1+D_1\nabla^2-\lambda_j)(\alpha-2\lambda_j)^{-1}\chi\cdot s_j^{-1}\end{aligned} \tag{3.14}$$

the eigenvectors $\mathbf{u}$ can be scaled differently. The most general vector $\mathbf{q}(\mathbf{x})$ can be expressed as superposition:

$$\mathbf{q}(x)=\begin{pmatrix}O_1^{(1)}\\ O_2^{(1)}\end{pmatrix}\xi(\mathbf{x})+\begin{pmatrix}O_1^{(2)}\\ O_2^{(2)}\end{pmatrix}\eta(\mathbf{x})=\mathbf{O}^{(1)}\xi(\mathbf{x})+\mathbf{O}^{(2)}\eta(\mathbf{x}). \tag{3.15}$$

Using the property

$$\bar{\mathbf{O}}^{(j)}\mathbf{O}^{(j')}=\delta_{jj'} \tag{3.16}$$

we obtain $\xi(\mathbf{x})$ and $\eta(\mathbf{x})$ from (3.15) in the form

$$\xi(\mathbf{x})=\bar{\mathbf{O}}^{(1)}\mathbf{q}(\mathbf{x}) \tag{3.17}$$

and

$$\eta(\mathbf{x})=\bar{\mathbf{O}}^{(2)}\mathbf{q}(\mathbf{x}). \tag{3.18}$$

This allows us to express the functional derivative $\delta/\delta q_i(\mathbf{x})$ in the form

$$\begin{aligned}\delta/\delta q_i(\mathbf{x})=&\int dx'\left(\delta/\delta\xi(\mathbf{x}')\right)\bar{O}_i^{(1)}\delta(\mathbf{x}-\mathbf{x}')\\ &+\int dx'\left(\delta/\delta\xi(\mathbf{x}')\right)\bar{O}_i^{(2)}\delta(\mathbf{x}-\mathbf{x}')\end{aligned} \tag{3.19}$$

or in short

$$\delta/\delta q_i(\mathbf{x})=\bar{O}_i^{(1)}\delta/\delta\xi(\mathbf{x})+\bar{O}_i^{(2)}\delta/\delta\eta(\mathbf{x}). \tag{3.20}$$

§ 4. Transformation of the Fokker-Planck Equation to New Mode Configuration

We want to treat that case explicitly in which λ is real and in which one mode gets unstable, i.e. $\lambda_1\geqq 0$, whereas $\lambda_2<0$ so that this mode is still stable. We first transform the Fokker-Planck equation (2.4) to the new modes amplitudes $\xi(\mathbf{x})$, $\eta(\mathbf{x})$. The linear part of the drift coefficients

$$\int\left(\delta/\delta q_1(\mathbf{x})\right)\mathbf{K}_1\mathbf{q}\,d^3x+\int\left(\delta/\delta q_2(\mathbf{x})\right)\mathbf{K}_2\mathbf{q}\,d^3x \tag{4.1}$$

is transformed by means of (3.15) and (3.17)–(3.20) to

$$\begin{aligned}&\int\left(\left(\delta/\delta\xi_1(\mathbf{x})\right)\bar{\mathbf{O}}^{(1)}+\left(\delta/\delta\eta(\mathbf{x})\right)\bar{\mathbf{O}}^{(2)}\right)\\ &\cdot\left(\lambda_1\mathbf{O}^{(1)}\xi(\mathbf{x})+\lambda_2\mathbf{O}^{(2)}\eta(\mathbf{x})\right)dx^3\end{aligned} \tag{4.2}$$

which by means of (3.12) reduces to

$$\int\left(\delta/\delta\xi(\mathbf{x})\right)\lambda_1\xi(\mathbf{x})d^3x+\int\left(\delta/\delta\eta(\mathbf{x})\right)\lambda_2\eta(\mathbf{x})d^3x. \tag{4.3}$$

The nonlinear part containing g transforms as

$$\begin{aligned}&\int\left(\delta/\delta q_1(\mathbf{x})-\delta/\delta q_2(\mathbf{x})\right)g(q_1,q_2)d^3x\\ &=\int\left(\delta/\delta\xi(\mathbf{x})\right)Q_1g\,d^3x+\int\left(\delta/\delta\eta(\mathbf{x})\right)Q_2g\,d^3x\end{aligned} \tag{4.4}$$

where $Q_j(\nabla)=\bar{O}_1^{(j)}-\bar{O}_2^{(j)}$ and g has now the form

$$g(q_1,q_2)=2a\big(O_1^{(1)}\xi(\mathbf{x})+O_1^{(2)}\eta(\mathbf{x})\big)\big(O_2^{(1)}\xi(\mathbf{x})+O_2^{(2)}\eta(\mathbf{x})\big)$$
$$+\frac{b}{a}\big(O_1^{(1)}\xi(\mathbf{x})+O_1^{(2)}\eta(\mathbf{x})\big)^2$$
$$+\big(O_1^{(1)}\xi(\mathbf{x})+O_1^{(2)}\eta(\mathbf{x})\big)^2\big(O_2^{(1)}\xi(\mathbf{x})+O_2^{(2)}\eta(\mathbf{x})\big)$$
$$\equiv\hat{g}(\xi,\eta). \tag{4.5}$$

Similarly the differential operators which determine the diffusion terms of the Fokker-Planck equation transform as

$$\delta^2/\delta q_j^2=\big(\bar{O}_j^{(1)}\delta/\delta\xi(\mathbf{x})+\bar{O}_j^{(2)}\delta/\delta\eta(\mathbf{x})\big)^2, \tag{4.6}$$

$$\delta^2/\delta q_1\delta q_2=\big(\bar{O}_1^{(1)}\delta/\delta\xi(\mathbf{x})+\bar{O}_1^{(2)}\delta/\delta\eta(\mathbf{x})\big)$$
$$\cdot\big(\bar{O}_2^{(1)}\delta/\delta\xi(\mathbf{x})+\bar{O}_2^{(2)}\delta/\delta\eta(\mathbf{x})\big), \tag{4.7}$$

and

$$\big(\nabla\delta/\delta q_j(\mathbf{x})\big)^2=\big(\nabla\big(\bar{O}_j^{(1)}\delta/\delta\xi(\mathbf{x})+\bar{O}_j^{(2)}\delta/\delta\eta(\mathbf{x})\big)\big)^2$$
$$=\big(\bar{O}_j^{(1)}\nabla\delta/\delta\xi(\mathbf{x})+\bar{O}_j^{(2)}\nabla\delta/\delta\eta(\mathbf{x})\big)^2. \tag{4.8}$$

As can be shown selfconsistently we may confine ourselves to the following drift coefficients

$$\hat{D}_{11}=2a+2ab \tag{4.9}$$

$$\hat{D}_{12}=\hat{D}_{22}=2ab, \tag{4.10}$$

i.e. we neglect the dependence of those terms on the coordinates q.

We now proceed to treat a more specific situation. We assume that we are near the threshold (i.e. closely below, at or above it) so that the mode which gets unstable first for a certain wave number plays a dominant role. This suggests similar to considerations in laser physics or in hydrodynamics to write $\xi(\mathbf{x})$ in the form

$$\xi(\mathbf{x})=\sum_{|\mathbf{k}|=k_c}\xi_{\mathbf{k}}(\mathbf{x})\chi_{\mathbf{k}}(\mathbf{x})+\sum_{|\mathbf{k}|\neq k_c}\xi_{\mathbf{k}}(\mathbf{x})\,\chi_{\mathbf{k}}(\mathbf{x}) \tag{4.11}$$

The first summation runs over wave vectors $\mathbf{k}$ which have the same absolute value, k_c, but which differ still with respect to their direction. The second sum contains the stable modes which are needed as virtual states and are eliminated adiabatically influencing the stability of the "unstable" modes.

$\xi_{\mathbf{k}}(\mathbf{x})$ is assumed to be a slowly varying function.

Because we have for each $\mathbf{k}$ two eigenvalues $\lambda_{1,2}$ one of which is close to 0 and connected with ξ, while the other is negative and connected with η, we also decompose η in the form

$$\eta(\mathbf{x})=\sum_{\mathbf{k}}\eta_{\mathbf{k}}(\mathbf{x})\,\chi_{\mathbf{k}}(\mathbf{x}). \tag{4.12}$$

If $\chi_{\mathbf{k}}$ is a complex function it is understood that

$$\chi_{\mathbf{k}}^*=\chi_{-\mathbf{k}} \quad \text{and} \quad \xi_{-\mathbf{k}}=\xi_{\mathbf{k}}^*;\ \eta_{-\mathbf{k}}=\eta_{\mathbf{k}}^*.$$

To evaluate the expressions (4.4), (4.6) to (4.8) explicitly we now recall that we have to apply the operators O to $\xi(\mathbf{x})$ and $\eta(\mathbf{x})$. Because ξ and $\eta(\mathbf{x})$ are, according to (4.11) and (4.12), a superposition of a slowly varying function times a rapidly varying function we may neglect the derivatives of the slowly varying function compared to those of $\chi_{\mathbf{k}}$ (with one exception explained below). Thus we evaluate these expressions for $\chi_{\mathbf{k}}$ only.

The critical value b_c is determined by the requirement $\lambda_1=O$. The first critical mode is determined by the condition that b_c is a minimum

$$b_c=(D_1k^2+1)(D_2k^2+a^2)/(D_2k^2). \tag{4.13}$$

After a short calculation we find

$$k^2=k_c^2=a(D_1D_2)^{-1/2}. \tag{4.14}$$

For the following it is convenient to introduce new quantities by

$$D_1k_c^2=a(D_1/D_2)^{1/2}=a\mu, \tag{4.15}$$

and

$$D_2k_c^2=a\mu^{-1}, \tag{4.16}$$

where we have used the abbreviation

$$(D_1/D_2)^{1/2}=\mu \tag{4.17}$$

so that b_c can be written in the form

$$b=b_c=(1+a\mu)^2. \tag{4.18}$$

For what follows we need the expansion of λ_1 around $b=b_c$ and $k=k_c$. For $k=k_c$ we obtain

$$\lambda_1=(b-b_c)(1+a^2-\mu^2-a\mu^3)^{-1}+O\big((b-b_c)^2\big). \tag{4.19}$$

On the other hand, at $b=b_c$, the expansion of λ_1 with respect to $(\nabla^2+k_c^2)$ yields

$$\lambda_1'\xi\approx 4a\mu\big((1-\mu^2)(1+a\mu)k_c^2\big)^{-1}\nabla^2\xi. \tag{4.20}$$

Here it is understood that ξ is slowly varying and the rapidly variation is projected out of (4.20). In total, we shall thus use

$$\lambda_1(b,\nabla)\approx\lambda_0+\lambda^{(1)}\nabla^2, \tag{4.20a}$$

where λ_0 is given by (4.19) and $\lambda^{(1)}\nabla^2$ by (4.20).

The corresponding eigenvalue λ_2 is found to yield (for $k=k_c$)

$$\lambda_2=\alpha=a\mu^{-1}(\mu^2-1)(1+a\mu)<0. \tag{4.21}$$

Using (3.13) we find the following expressions for the O's

1. $j=1$, $\lambda_1\approx 0 \quad |k|=k_c$

$$O_1^{(1)}=-a\big(\mu(1+a\mu)\big)^{-1}s_1 \tag{4.22}$$

$$O_2^{(1)}=1\cdot s_1 \tag{4.23}$$

$$\bar{O}_1^{(1)}=\mu(1+a\mu)\big(a(\mu^2-1)\big)^{-1}\cdot s_1^{-1} \tag{4.24}$$

$$\bar{O}_2^{(1)}=\mu^2(\mu^2-1)^{-1}s_1^{-1}. \tag{4.25}$$

2. $j=2$, $\lambda_2=\alpha<0$, $|k|=k_c$

$$O_1^{(2)}=-a\mu(1+a\mu)^{-1}s_2 \tag{4.26}$$

$$O_2^{(2)}=1\cdot s_2 \tag{4.27}$$

$$\bar{O}_1^{(2)}=\mu(1+a\mu)(a(1-\mu^2))^{-1}s_2^{-1} \tag{4.28}$$

$$\bar{O}_2^{(2)}=(1-\mu^2)^{-1}s_2^{-1}. \tag{4.29}$$

Later on, we also need the O's for $k=0$ and $k=2k_c$. Since they can be calculated in a completely analogous manner, we do not exhibit them explicitly.

One readily verifies that these O's guarantee that the $\mathbf{u}$'s are orthonormal and are eigenvectors to K_0. The scaling factors s_1, s_2 will be put equal 1 which amounts to choosing the concentration $N(\mathbf{x})$ as a reference. (Another choice would be $O_1^{(1)}=O_2^{(2)}=1$, which prefers $M(\mathbf{x})$ as reference.) Using (4.3), (4.4), (4.6), (4.7), (4.8), (4.11), (4.12) the Fokker-Planck equation acquires the form:

$$\dot{F}=\{(\mathrm{I})+(\mathrm{II})+(\mathrm{III})\}F, \tag{4.30}$$

where

$$(\mathrm{I})=-\int d^3x\sum_{\mathbf{k}}(\delta/\delta\xi_{\mathbf{k}}(\mathbf{x}))\{\lambda_1\xi_{\mathbf{k}}+Q_1\tilde{g}_{\mathbf{k}}(\xi,\eta)\}. \tag{4.31}$$

$\lambda_1=\lambda_1(V,\mathbf{k})$ will be specified below, $Q_1=Q_1(\mathbf{k})$, and

$$\begin{aligned}\tilde{g}_{\mathbf{k}}(\xi,\eta)=&\sum_{\mathbf{k}',\mathbf{k}''}I_{\mathbf{k}\mathbf{k}'\mathbf{k}''}(c_1\xi_{\mathbf{k}'}\xi_{\mathbf{k}''}+c_2\xi_{\mathbf{k}'}\eta_{\mathbf{k}''}+c_3\eta_{\mathbf{k}'}\eta_{\mathbf{k}''})\\&+\sum_{\mathbf{k}',\mathbf{k}'',\mathbf{k}'''}J_{\mathbf{k}\mathbf{k}'\mathbf{k}''\mathbf{k}'''}(a_1\xi_{\mathbf{k}'}\xi_{\mathbf{k}''}\xi_{\mathbf{k}'''}+a_2\xi_{\mathbf{k}'}\xi_{\mathbf{k}''}\eta_{\mathbf{k}'''}\\&+a_3\xi_{\mathbf{k}'}\eta_{\mathbf{k}''}\eta_{\mathbf{k}'''}+a_4\eta_{\mathbf{k}'}\eta_{\mathbf{k}''}\eta_{\mathbf{k}'''})\end{aligned} \tag{4.32}$$

with

$$I_{\mathbf{k}\mathbf{k}'\mathbf{k}''}=\int\chi_{\mathbf{k}}^*\chi_{\mathbf{k}'}\chi_{\mathbf{k}''}d^3x, \tag{4.33}$$

$$J_{\mathbf{k}\mathbf{k}'\mathbf{k}''\mathbf{k}'''}=\int\chi_{\mathbf{k}}^*\chi_{\mathbf{k}'}\chi_{\mathbf{k}''}\chi_{\mathbf{k}'''}d^3x \tag{4.34}$$

and $c_\nu=c_{\nu\mathbf{k}'\mathbf{k}''}$, $a_\nu=a_{\nu\mathbf{k}'\mathbf{k}''\mathbf{k}'''}$

$\eta_{-\mathbf{k}}=\eta_{\mathbf{k}}^*$, $\xi_{\mathbf{k}}=\xi_{\mathbf{k}}^*$.

$$(\mathrm{II})=-\int d^3x\sum_{\mathbf{k}}(\delta/\delta\eta_{\mathbf{k}}(\mathbf{x}))\{\lambda_2\eta_{\mathbf{k}}+Q_2\tilde{g}_{\mathbf{k}}\}. \tag{4.35}$$

$$\begin{aligned}(\mathrm{III})=&\int d^3x\{G_{11}\sum_{\mathbf{k}}\delta^2/\delta\xi_{\mathbf{k}}\delta\xi_{\mathbf{k}}^*-G_{12}\sum_{\mathbf{k}}\delta^2/\delta\xi_{\mathbf{k}}\delta\eta_{\mathbf{k}}^*\\&+G_{22}\sum_{\mathbf{k}}\delta^2/\delta\eta_{\mathbf{k}}\delta\eta_{\mathbf{k}}^*\}\end{aligned} \tag{4.36}$$

where the coefficients G_{ij} depend on $\mathbf{k}$ and are specified below.

§ 5. Adiabatic Elimination

The resulting Fokker-Planck equation has the form

$$\dot{F}=(L_1+L_2+L_3)F, \tag{5.1}$$

where the Liouville operators are as follows

$$L_1=L_1(\delta_\xi,\xi,\eta),\quad \text{only } \delta_\xi \text{ with } |k|=k_c, \tag{5.2}$$

$$L_2=L_2(\delta_\xi,\delta_\eta,\xi,\eta),\quad \text{only } \delta_\xi \text{ with } |k|\neq k_c, \tag{5.3}$$

$$L_3=L_3(\delta_\xi,\delta_\eta,\xi,\eta),\text{ with mixed }\delta\text{'s}. \tag{5.4}$$

δ_ξ, δ_η are abbreviations for the functional derivatives with respect to ξ and η, respectively. We assume that L_2 contains the operators δ_ξ, δ_η linearly or quadratically standing on the left hand side of the whole expression. Similarly (5.4) is assumed to be a bilinear function in δ_ξ and δ_η, both derivatives again standing on the left of the whole expression L_2. We now try to eliminate the damped modes assuming that these modes follow the motion of the unstable modes adiabatically. This suggests to apply a similar approach as in the Born-Oppenheimer approximation by making the hypothesis

$$F=f(\xi_c)\,h(\eta;\xi_c;\xi_s),\quad c=\text{critical},\ s=\text{stable} \tag{5.5}$$

where h is assumed to be a slowly varying function of ξ_c, so that in a first approximation we may neglect the derivatives of this function with respect to ξ_c. The function h is assumed normalized in the sense

$$\int\{D\eta\,D\xi_s\}\,h(\eta;\xi_s;\xi_c)=1. \tag{5.6}$$

We require that $h(\xi,\eta)$ fulfills the Fokker-Planck equation

$$L_2h(\eta;\xi)=0. \tag{5.7}$$

In order to find an equation for $f(\xi)$ we insert (5.5) into (5.1) and integrate over ξ_s and η. Using (5.7) and the properties of (5.3) we find

$$\dot{f}=\int L_1h\,D\xi_s\,D\eta\cdot f. \tag{5.8}$$

Our next task is to solve (5.7). Since we expect that the mode amplitudes ξ_s are still small (though finite due to fluctuations!) in a region somewhat above threshold, we keep in the following only the leading terms in ξ_c. Because for stability at least cubic terms are needed in the resulting drift terms, we keep in L_2 just terms quadratic in ξ_c. We further replace V by $\mathbf{k}$ in (3.5). Thus L_2 has the form

$$\begin{aligned}L_2=&-\int d^3x\sum_{\substack{\mathbf{k}\\|k|\neq k_c}}\delta/\delta\xi_{\mathbf{k}}(\mathbf{x})\{\lambda_1(\mathbf{k})\,\xi_{\mathbf{k}}(\mathbf{x})\\&+\sum_{\substack{\mathbf{k}',\mathbf{k}''\\|\mathbf{k}'|=|\mathbf{k}''|=k_c}}I_{\mathbf{k}\mathbf{k}'\mathbf{k}''}Q_1(\mathbf{k})\,c_{1\mathbf{k}'\mathbf{k}''}\,\xi_{\mathbf{k}'}\,\xi_{\mathbf{k}''}\}\\&+\int d^3x\sum_{\substack{\mathbf{k}\\|k|\neq k_c}}G_{11}\,\delta^2/\delta\xi_{\mathbf{k}}\,\delta\xi_{\mathbf{k}}^*\\&-\int d^3x\sum_{\mathbf{k}}\delta/\delta\eta_{\mathbf{k}}(\mathbf{x})\{\lambda_2(k)\,\eta_{\mathbf{k}}(\mathbf{x})\end{aligned}$$

$$+\sum_{\substack{\mathbf{k}'\mathbf{k}''\\|k'|=|k''|=k_c}} I_{\mathbf{k}\mathbf{k}'\mathbf{k}''} Q_2(\mathbf{k}) c_1 \xi_{\mathbf{k}'} \xi_{\mathbf{k}''}\}$$

$$+\int d^3x \sum_{\mathbf{k}} G_{22}\, \delta^2/\delta\eta_{\mathbf{k}}\, \delta\eta^*_{\mathbf{k}} \tag{5.9}$$

where we have neglected the cross term G_{12}. (It is not difficult, however, to find the exact solution of (5.7), even if $G_{12}\neq 0$.) The solution of (5.7) is given by a product of Gaussian integrals, where $\xi_{\mathbf{k}}(|k|\neq k_c)$ is centered around

$$\xi_{\mathbf{k}} = -\lambda_1(\mathbf{k})^{-1} \sum_{\substack{\mathbf{k}'\mathbf{k}''\\|\mathbf{k}'|=|\mathbf{k}''|=k_c}} I_{\mathbf{k}\mathbf{k}'\mathbf{k}''} Q_1(\mathbf{k})\, c_{1\,\mathbf{k}'\mathbf{k}''}\, \xi_{\mathbf{k}'}\, \xi_{\mathbf{k}''} \tag{5.10}$$

and $\eta_{\mathbf{k}}$ correspondingly (with λ_1 replaced by λ_2 and Q_1 by Q_2). We now consider L_1, which we obtain as follows: In (4.31) the sum over $\mathbf{k}$ is now restricted to $|\mathbf{k}|=k_c$. In $\tilde{g}_k$ (4.32) we keep only terms, which after elimination of the stable modes give rise to terms up to third order in ξ_c. Furthermore, the diffusion terms of L_1 are obtained from (4.36) by keeping only the first sum$\propto G_{11}$, and here again only the terms with $|\mathbf{k}|=k_c$.

The evaluation of (5.8) is now rather simple. Since the explicit formula is lengthy, we just quote the final result. As one may show, the whole result of the integration in (5.8) essentially amounts to replacing ξ_s and η in L_1 by (5.10) and the corresponding expression in η. The final result is exhibited in the next paragraph.

§ 6. Final Fokker-Planck Equation for $\xi_{\mathbf{k}}(\mathbf{x})$

This equation reads

$$\dot{f} = -\int d^3x \sum_{\mathbf{k}} \left[(\delta/\delta\xi_{\mathbf{k}}(\mathbf{x}))\{\lambda_1(V)\xi_{\mathbf{k}}(\mathbf{x}) + H_{\mathbf{k}}(\xi)\}\right.$$

$$\left. - G_{11} \sum_{\mathbf{k}} \delta^2/\delta\xi_{\mathbf{k}}\delta\xi^*_{\mathbf{k}}\right] f \tag{6.1}$$

where all sums are now restricted to $|\mathbf{k}|=k_c$, without being explicitly indicated. $\lambda_1(V)$ is given explicitly by (4.20a) with (4.20), (4.19). We have further

$$G_{11} = 2\big(a(1-\mu^2)^2\big)^{-1} \cdot \mu^2(1+a\mu)^2$$

and

$$H_{\mathbf{k}}(\xi) = \sum_{\mathbf{k}'\mathbf{k}''} I_{\mathbf{k}'\mathbf{k}''\mathbf{k}'''}\, \bar{c}_1\, \xi_{\mathbf{k}'}(\mathbf{x})\, \xi_{\mathbf{k}''}(\mathbf{x})$$

$$- \sum_{\mathbf{k}'\mathbf{k}''\mathbf{k}'''} \bar{a}_1\, J_{\mathbf{k}\mathbf{k}'\mathbf{k}''\mathbf{k}'''}\, \xi_{\mathbf{k}'}(\mathbf{x})\, \xi_{\mathbf{k}''}(\mathbf{x})\, \xi_{\mathbf{k}'''}(\mathbf{x}). \tag{6.2}$$

Here

$$\bar{c}_1 = \big(\mu(1+a\mu)(\mu^2-1)\big)^{-1} \cdot (1-a\mu)$$

and

$$\bar{a}_1\, J_{\mathbf{k}\mathbf{k}'\mathbf{k}''\mathbf{k}'''} \equiv \bar{a}_{1\,\mathbf{k}\mathbf{k}'\mathbf{k}''\mathbf{k}'''}\, J_{\mathbf{k}\mathbf{k}'\mathbf{k}''\mathbf{k}'''}$$

$$= a\big(\mu(1-\mu^2)(1+a\mu)^2\big)^{-1} J_{\mathbf{k}\mathbf{k}'\mathbf{k}''\mathbf{k}'''}$$

$$+ 2 \sum_{\hat{\mathbf{k}}} I_{\mathbf{k}\mathbf{k}'\hat{\mathbf{k}}}\, I_{\hat{\mathbf{k}}\mathbf{k}''\mathbf{k}'''}\, Q(\mathbf{k}_c)\{c_{1\,\mathbf{k}'\hat{\mathbf{k}}}\, \lambda_1(\hat{\mathbf{k}})^{-1}\, Q_1(\hat{\mathbf{k}}) \cdot c_{1\,\mathbf{k}''\mathbf{k}'''}$$

$$+ c_{2\,\mathbf{k}'\hat{\mathbf{k}}}\, \lambda_2(\hat{\mathbf{k}})^{-1}\, Q_2(\hat{\mathbf{k}})\, c_{1\,\mathbf{k}''\mathbf{k}'''}\} \tag{6.3}$$

$\hat{\mathbf{k}}$ is not restricted to $|\hat{\mathbf{k}}|=k_c$!

For a discussion of the evolving spatial structures the "selection rules" inherent in I, (4.33), and J, (4.34), are important. One readily verifies:

a) in one dimension:

$I=0$ for no boundary conditions, i.e. the $\chi_{\mathbf{k}}$'s are plane waves;

$I\approx 0$ for $\chi_{\mathbf{k}} \propto \sin kx$ and $k \gg 1$.

Further

$J_{\mathbf{k}\mathbf{k}'\mathbf{k}''\mathbf{k}'''} = J \neq 0$ only if two pairs of k's out of $\mathbf{k},\mathbf{k}',\mathbf{k}'',\mathbf{k}'''$ satisfy:

$$k_1 = -k_2 = -k_c$$
$$k_3 = -k_4 = -k_c$$

if plane waves are used, or $k=k'=k''=k'''=k_c$ if $\chi_k \propto \sin kx$.

We have evaluated $\bar{a}_1$ explicitly for plane waves. The resulting coefficient A in Eq. (1.3) then reads:

$$A = \big(9(1-\mu^2)\,\mu^3(1+a\mu)^2\, a\big)^{-1}$$

$$\cdot(-8a^3\mu^3 + 5a^2\mu^2 + 20a\mu - 8).$$

Note that for sufficiently big $a\mu$, the coefficient A becomes negative. A closer inspection shows, that under this condition the mode with $k=0$ approaches a marginal situation which requires then to consider the modes with $k=0$ (and $|\mathbf{k}|=2k_c$) as unstable modes.

b) in three dimensions, thin layer without horizontal boundaries

$$\chi_{\mathbf{k}} = \mathfrak{N}_0 \sin(\pi z/d) \exp(ik_x x + ik_y y).$$

We put $(k_x, k_y)=\hat{\mathbf{k}}$. Then $I_{\mathbf{k}\mathbf{k}'\mathbf{k}''} = I \neq 0$ if $\hat{k}, \hat{k}', \hat{k}''$ form a triangel with equal side lengths. (This triangel forms a basis of the hexagons [30, 36].) $J_{\mathbf{k}\mathbf{k}'\mathbf{k}''\mathbf{k}'''} = J \neq 0$ if $\hat{k}, \hat{k}', \hat{k}'', \hat{k}'''$ form a parallelogram with two pairs of opposite sides so that

$$\hat{\mathbf{k}}_1 = -\hat{\mathbf{k}}_2$$
$$\hat{\mathbf{k}}_3 = -\hat{\mathbf{k}}_4.$$

We note in conclusion that a number of procedures are available to solve the Eqs. (1.3) and (1.4). The detailed results will be published in a subsequent paper.

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Note Added in Proof. After submission for publication of this paper the following somewhat related papers came to our attention: G. Nicolis, P. Allen and A. van Nypelseer, Progr. Theoret. Physics, **52**, 1481 (1974); and M. Malek-Mansour and G. Nicolis, preprint, February 1975, give a detailed discussion of birth-death processes. They include diffusion in a way different from our treatment.
Y. Kuramoto and T. Tsusuki, Progr. Theor. Phys. **52**, 1399 (1974) and preprint, 1975, treat small-band excitations of the one-dimensional Prigogine-Lefever-Nicolis model and of a general two-component system without fluctuations.

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