Nonequilibrium Phase Transitions and Chemical Reactions

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The principal bifurcations occurring in reaction-diffusion systems away from equilibrium are reviewed. The effect of fluctuations on the bifurcation is investigated using a master equation approach. The following situations are envisaged:

(i) All-or-none transitions in bistable spatially homogeneous systems. The behavior of the variance below and at the bifurcation point is discussed. The condition of coexistence of simultaneously stable states is shown to yield a relation between parameters which differs from the Maxwell type construction inferred from the deterministic equations. It is pointed out that in the thermodynamic limit the master equation displays two distinct solutions.

(ii) Hopf bifurcations leading to limit cycles in spatially homogeneous systems. Numerical results are reported illustrating the structure of the "probability crater" descriptive of the limit cycle. It is suggested that in the thermodynamic limit, in addition to the static solution given by the probability crater there is a one-parameter family of time-dependent solutions rotating along the limit cycle.

(iii) Spatially distributed systems. The effect of diffusion on all-or-none transitions is discussed using an extension of mean-field theory in conjunction with Monte-Carlo simulations.

§ 1. Introduction

The emergence of ordered behavior in systems far from thermodynamic equilibrium has received considerable attention recently. This paper is devoted to the analysis of a particular class of such systems, namely systems involving nonlinear chemical reactions of the autocatalytic or cross-catalytic type and diffusion. It is a matter of observation that the dynamics of these systems is amenable to a set of phenomenological laws of evolution for a limited number of macroscopic observables, typically the concentrations $\overline{x}_i$ of the active chemical intermediates. Assuming Fickian diffusion in a dilute mixture and constant temperature throughout, the evolution equations of these variables take the form:

$$\frac{\partial \overline{x}_i}{\partial t}=v_i(\overline{x}_1, \cdots, \overline{x}_n; \lambda)+D_i\nabla^2\overline{x}_i . \quad (i=1, \cdots, n) \qquad (1\cdot 1)$$

D_i are diffusion coefficients, v_i the overall rate of change of $\bar{x}_i$ arising from the chemical reactions involving constituent i, and λ stand for a set of parameters (rate constants, concentrations of buffered chemicals) descriptive of the system.

Equations (1·1) have been investigated extensively in the last decade.[1] Under natural boundary conditions—zero flux or periodic—they have been shown to present a number of *transition phenomena* around the spatially uniform and time-independent state satisfying (1·1) and reducing to the law of mass action at equilibrium. These transitions occur through a *bifurcation* mechanism, which usually involves an exchange of stability between an initially stable "reference" solution and a new stable branch of solutions. The situation is depicted in Fig. 1.

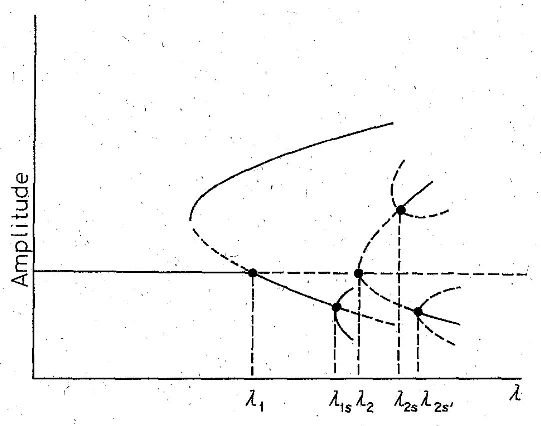

Fig. 1. Illustration of the phenomenon of cascading bifurcations.

The most common bifurcations are those leading (i) to multiple steady states and hysteresis without any change in spatial and temporal symmetries, (ii) to a time symmetry-breaking associated with the formation of time-periodic solutions of the limit-cycle type, and (iii) to a space symmetry-breaking associated with the emergence of space order. The last two types of behavior are possible in systems involving at least two coupled variables.

Now, the occurrence of transitions extending over macroscopic space and time scales suggests the existence of long-range correlations ensuring coherence within the medium, as soon as one approaches and crosses the bifurcation point. Because of this, we expect that the local state of affairs will no longer be determined exclusively by the immediate neighborhood of a particular volume element, as Eq. (1·1) would imply. Rather, each element of the system feels the cumulative effect of distant parts which ultimately introduce deviations from the phenomenological behavior. In more precise terms, we expect that the *fluctuations,* which are damped when the state of the system enjoys asymptotic stability, attain macroscopic values in the vicinity of and past the bifurcation points.

Our principal goal in this paper is to analyze the structure of these fluctuations for the three types of bifurcation reviewed above. Fluctuations will be modelled as *Markov processes* in appropriate phase space. For instance, dividing the reaction volume into spatial cells and considering as variables the numbers of particles $X_{i\alpha}$ of species i within cell α, one will have a multivariate probability $P(X_{i\alpha}, t)$ obeying a master equation generated by the forward Kolmogorov equation:[2]

$$\frac{dP(X_{i\alpha}, t)}{dt} = \sum_{\alpha}\{\sum_{X'_{i\alpha}} W(X'_{i\alpha}|X_i)P(X'_{i\alpha}, t) + \sum_i d_i((X_{i\alpha}+1) \times (P(X_{i\alpha-1}-1, X_{i\alpha}+1, t) + P(X_{i\alpha}+1, X_{i\alpha+1}-1, t)) - 2X_{i\alpha}P(X_{i\alpha}, t))\}, \tag{1·2}$$

where d_i are the diffusion rates across cells and W the transition probabilities per unit time for the chemical porcesses. Here diffusion is modelled as a random walk, whereas chemical reactions are viewed as *birth and death* processes, since they correspond to the appearance or disappearance of a small number of molecules (usually one) at a time.

An interesting limiting case refers to continuous Markov processes. The forward Kolmogorov equation takes in this case the form

$$\frac{\partial P(x,t)}{\partial t} = -\frac{\partial}{\partial x}V(x)P(x,t) + \frac{1}{2N}\frac{\partial^2}{\partial x^2}D(x)P(x,t) + (\text{spatial diffusion terms}), \tag{1·3}$$

where N is the size, x the intensive variable associated to X and $V(x)$, $D(x)$ the first two transition moments of $W(X'|X)$. This equation is usually referred to as nonlinear Fokker-Planck equation. Its relation to (1·2) has recently been investigated by Horsthemke and Brenig;[3] see also Hänggi.[4]

An important property underlying Eq. (1·2) as well as the passage from Eq. (1·2) to Eq. (1·3) is Kurtz's theorem.[5] It asserts that in the thermodynamic limit, $N\to\infty$ each individual realization of the stochastic process remains in a vicinity of the phenomenological trajectory, Eq. (1·1), for all finite times provided the initial condition is identical for both trajectories. Moreover, it provides bounds for the difference between stochastic and deterministic trajectories as well as between the trajectories associated to the discrete and continuous Markov process, Eqs. (1·2) and (1·3). As we shall see later however, Kurtz's theorem is perfectly compatible with the occurrence of giant fluctuations around states lacking asymptotic stability.

We now treat, successively, the onset of cooperative behavior of fluctuations as the system approaches and then crosses a bifurcation point leading to bistability and limit-cycle behavior. In § 4 we discuss the effect of spatial diffusion, whereas § 5 is devoted to some general comments.

§ 2. All-or-none transitions in spatially uniform systems

The simplest bifurcation predicted by equations of evolution of the reaction-diffusion type is in systems involving one internal variable and a cubic rate law. This phenomenon is best illustrated by the following chemical model due to Schlögl:[6]

$$\mathrm{A}+2\mathrm{X} \underset{k_2}{\overset{k_1}{\rightleftarrows}} 3\mathrm{X}$$
$$\mathrm{X} \underset{k_4}{\overset{k_3}{\rightleftarrows}} \mathrm{B}\,. \tag{2·1}$$

A and B are controlled from outside and play the role of "pumping parameters". The system is supposed to remain uniform in space (e.g., through adequate stirring), and this will enable us to neglect diffusion.

As is well known, the behavior of a cubic is controlled completely by two parameters. Hence we define the following scaled quantities:

$$X=N(1+\overline{x}), \quad k_1A/k_2=3N, \quad k_3/k_2=(3+\delta)N^2$$
$$k_4B/k_2=(1+\delta')N^3, \quad \tau=k_2N^2t\,, \tag{2·2}$$

where N is proportional to the size of the system. The rate equation for model (2·1) takes then the form:

$$\frac{d\overline{x}}{d\tau}=-\overline{x}^3-\delta\overline{x}+(\delta'-\delta)\,. \tag{2·3a}$$

It obviously derives from a macroscopic potential featured in catastrophe theory:[7]

$$\mathcal{V}(\overline{x})=\frac{\overline{x}^4}{4}+\delta\frac{\overline{x}^2}{2}+(\delta-\delta')\overline{x}\,. \tag{2·3b}$$

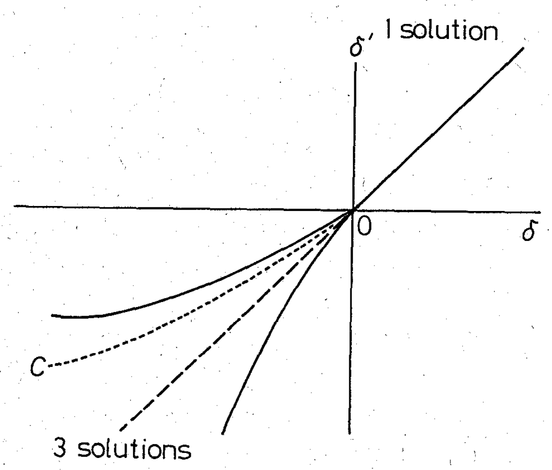

Fig. 2. Stability diagram for the Schlögl model (2.1).
0 = "cusp" singularity.
······ Coexistence line of stable steady states as given by master equation.
---- Coexistence line as given by Maxwell construction.

As δ, δ' move to negative values along the line $\delta=\delta'$ a bifurcation phenomenon takes place at the point $\delta=\delta'=0$ (see Fig. 2). For negative values of δ, δ' Eq. (2·3a) admits three steady-state solutions: the trivial state $\bar{x}_0=0$ which is unstable, and two non-trivial states $\bar{x}_\pm=\pm\sqrt{-\delta}$ which are stable. If on the other hand one moves into the multiple steady-state region away from the line $\delta=\delta'$, one encounters the phenomenon of hysteresis. In this section we want to analyze the behavior of fluctuations associated to bifurcation across the point $\delta=\delta'=0$, in the limit where the size of the system N gets large.

We first regard (2·1) as a Markov chain and write the master equation (1·2) in the form (cf. also (2·2)),

$$\begin{aligned}\frac{dP(X,\tau)}{d\tau}=&N^{-2}[X(X+1)(X-1)P(X+1,\tau)-X(X-1)(X-2)P(X,\tau)]\\&+3N^{-1}[(X-1)(X-2)P(X-1,\tau)-X(X-1)P(X,\tau)]\\&+(3+\delta)[(X+1)P(X+1,\tau)-XP(X,\tau)]\\&+(1+\delta')N[P(X-1,\tau)-P(X,\tau)].\end{aligned}\tag{2·4}$$

It is already of interest to point out that, despite the simplicity of model (2·1), Eq. (2·4) defines a rather non-classical Markov chain, mainly because of the unbounded character of the transition probabilities per unit time. For instance, it can be easily checked that the chain is not regular, in the sense that it may accomplish an infinity of steps in a finite time interval. To see this, one evaluates the sum of mean sojourn times of the various states[2]

$$\langle T\rangle=\sum_{X=0}^{\infty}\frac{1}{N^{-2}X(X-1)(X-2)+3N^{-1}X(X-1)+(3+\delta)X+(1+\delta')N}.\tag{2·5}$$

Because of the cubic and quadratic terms in the denominator, this series converges for any finite N: $\langle T\rangle<\infty$. What happens here is that infinity is an entrance boundary. Once there, the system is attracted very rapidly to a finite region of state space. Despite these features however, one can check that for any finite N the transition probabilities verify a theorem due to Karlin and Mc Gregor,[8] which guarantees both ergodicity of the process and uniqueness of the stationary probability distribution.

We proceed now to construct this steady-state distribution.[9),10)] A fortunate situation is that for model (2·1) this can be done exactly, through an integral representation of the generating function.[11)] From this one can evaluate the variance of X in the thermodynamic limit, $N\to\infty$. When the bifurcation point $\delta=\delta'=0$ is approached along the line $\delta=\delta'$ one finds

$$\lim_{N\to\infty}\frac{\langle(\delta X)^2\rangle}{N}\sim\frac{1}{|\delta|}.\tag{2·6a}$$

Thus, fluctuations are extensive although as $|\delta|\to 0$ they tend to diverge. The law of divergence is classical, a result due presumably to our assumption about the global character of fluctuations. On the other hand, at the bifurcation point $\delta=\delta'=0$ the fluctuations are not extensive:

$$\lim_{N\to\infty}\frac{\langle(\delta X)^2\rangle}{N^{3/2}}=\text{finite}. \tag{2·6b}$$

Still, in the limit $N\to\infty$ the first moment equation generated by Eq. (2·4) reduces to the phenomenological rate equation, in agreement with Kurtz's theorem.

Let us next focus on the region of coexistence of simultaneously stable states.[12] As expected, bistability is reflected by a two-humped probability distribution with peaks centered on the asymptotically stable solutions of Eq. (2·3a) and with a minimum on the unstable solution:

$$P=\phi(x)\exp N\mathcal{U}(x):\begin{cases}\left.\dfrac{d\mathcal{U}(x)}{dx}\right|_{\bar{x}_\pm}=0\,, & \left.\dfrac{d^2\mathcal{U}(x)}{dx^2}\right|_{\bar{x}_\pm}<0\,,\\ \left.\dfrac{d\mathcal{U}(x)}{dx}\right|_{\bar{x}_0=0}=0\,, & \left.\dfrac{d^2\mathcal{U}(x)}{dx^2}\right|_{\bar{x}_0=0}>0\,,\end{cases} \tag{2·7}$$

where x is an intensive variable associated to X.

If one requires the ratio of the two probability peaks to be of the order of unity, one finds a condition between parameters δ and δ' defining the line C on Fig. 2. Outside this "coexistence line" one of the two peaks is smaller than the other by a factor of the order of e^{-N}, and therefore disappears in the thermodynamic limit. The point is that the coexistence line is *not* the line $\delta=\delta'$ along which the phenomenological potential, Eq. (2·3b), has two equal-height extrema. We conclude that the "Maxwell convention" employed usually to determine the transition between multiple steady states does not reflect the correct structure of the probability distribution in the multiple steady state region. On the other hand even though the stochastic potential $\mathcal{U}(x)$ is different from the phenomenological potential $\mathcal{V}(x)$, they both predict the same critical behavior of fluctuations when the bifurcation point is approached from the *pretransitional* region (see Eq. (2·6a)). Note that in a formalism based on a nonlinear Fokker-Planck equation, Eq. (1·3), a similar discrepancy would arise according as one would include the x-dependence of the second transition moment $D(x)$[13] or one would argue in terms of a constant D.[14] Whatever the formalism used, all along the coexistence line C one finds a variance of the same order of magnitude as $\bar{x}_+$ or $\bar{x}_-$:

$$\lim_{N\to\infty}\frac{\langle(\delta X)^2\rangle}{N^2}=\text{finite}\quad(\neq 0)\,. \tag{2·8}$$

This introduces macroscopic deviations of the equations of evolution from the phenomenological form, Eq. (2·3a).

A question of considerable importance concerns the structure of the probability distribution, Eq. (2·7), in the thermodynamic limit $N \to \infty$. One can show[12] that each of the humps of the probability function collapses to a delta function in this limit. One gets therefore a stationary probability distribution of the form

$$P(x) = C_+ \delta(x - \overline{x}_+) + C_- \delta(x - \overline{x}_-), \tag{2·9}$$

where the weights C_+ and C_- sum to unity and are otherwise determined explicitly in terms of the stochastic potential $\mathcal{U}(x)$ and the preexponential factor $\phi(x)$ appearing in Eq. (2·7).

We see that a deep change takes place with respect to the Markov chain case (N finite), in the sense that $\overline{x}_+$ and $\overline{x}_-$ now seem to act as "absorbing boundaries", whereas all other states—including the unstable state—are inaccessible. As shown in the Appendix, both $\delta(x - \overline{x}_+)$ and $\delta(x - \overline{x}_-)$ satisfy the master equation independently, whereas their "mixture" gives the thermodynamic limit form of the steady-state probability distribution $P(x)$. The analogy with the Ising model is striking.

The results reported so far are all derived from the explicit solution of the master equation and from its properties in the limit $N \to \infty$. It would be desirable to develop systematic perturbative methods enabling us to tackle more complex situations not amenable to an exact solution. In a previous paper[11] we developed a singular perturbation analysis of the master equation in the vicinity of the bifurcation point. A similar method encompassing both the vicinity of the bifurcation point and the multiple steady-state region is reported in the Appendix. It enables us to treat the master equation in a way which parallels as closely as possible the bifurcation analysis at the phenomenological level.

§ 3. Bifurcation of limit cycles in spatially uniform systems

The stochastic theory of Hopf bifurcations leading to limit cycles is much more complicated than the theory discussed in the preceding section, because it involves at least two coupled state variables. For this reason, most of the analytic work performed so far is based on approximate solutions obtained by truncation procedures or by anticipating a Gaussian behavior for the fluctuations. One then finds a result similar to Eq. (2·6a) for the pretransitional behavior of the variances as the system approaches the bifurcation point. Moreover, as pointed out by Tomita et al.[15] one may define an "irreversible circulation of fluctuations" to characterize the breakdown of detailed balance condition associated with the onset of the limit cycle.

Contrary to § 2, it is not possible at this time to corroborate these approximate results by exact solutions of the stochastic equations. We therefore resort to computer simulations and to a systematic perturbative treatment of the master equations. Most of the results reported below refer to the limit cycle behavior of the Brusselator:[1)]

$$\begin{aligned} A &\longrightarrow X\,, \\ B+X &\longrightarrow Y+D\,, \\ 2X+Y &\longrightarrow 3X\,, \\ X &\longrightarrow E\,. \end{aligned} \tag{3·1}$$

A, B are controlled from outside. The system is maintained uniform in space by adequate stirring.

In order to realize the complexity of the stochastic problem associated with model (3·1) we consider, as in § 2, the underlying Markov chain. In other words, we consider the process to be a random walk in the phase space (X, Y) with variable transition probabilities. These are easily computed from the transition rates appearing in the master equation, Eq. (1·2). The result is:

$$\begin{aligned} \Pi(X,Y;X+1,Y) &= \frac{A}{W(X,Y)}\,, \\ \Pi(X,Y;X+1,Y-1) &= \frac{X(X-1)Y/N^2}{W(X,Y)}\,, \\ \Pi(X,Y;X-1,Y+1) &= \frac{BX/N}{W(X,Y)}\,, \\ \Pi(X,Y;X-1,Y) &= \frac{X}{W(X,Y)}\,, \end{aligned} \tag{3·2}$$

where

$$W(X,Y) = A + X(X-1)\,Y/N^2 + (B/N+1)\,X\,. \tag{3·3}$$

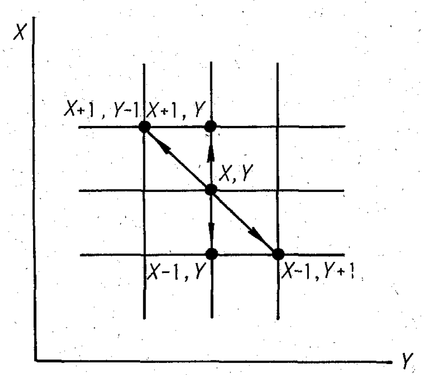

Fig. 3. Allowed transitions between states in the (X, Y) plane.

Figure 3 represents the allowed transitions in the phase space (X, Y).

We see that some of the transitions connect states that are not nearest neighbors, whence the mathematical difficulties in solving the problem. These peculiarities are to be connected with the fact that the limit cycle for the Brusselator tends to become triangular when the bifurcation parameter exceeds its critical value.

We now describe the results of a direct numerical simulation of the stochastic process described by (3·1) beyond the bifurcation point. As shown in Fig. 4, one obtains a *steady-state* probability function in the form of a crater-like surface centered on the limit cycle. The portions of the periodic trajectory that correspond to a slow motion are weighted by an absolute maximum of the probability, whereas the portions of fast motion give a much smaller peak. Actually, as shown analytically by Ebeling[17] on a non-chemical limit cycle example, in the three-dimensional representation of the probability crater the fast motion portion corresponds to a saddle rather than to a local maximum.

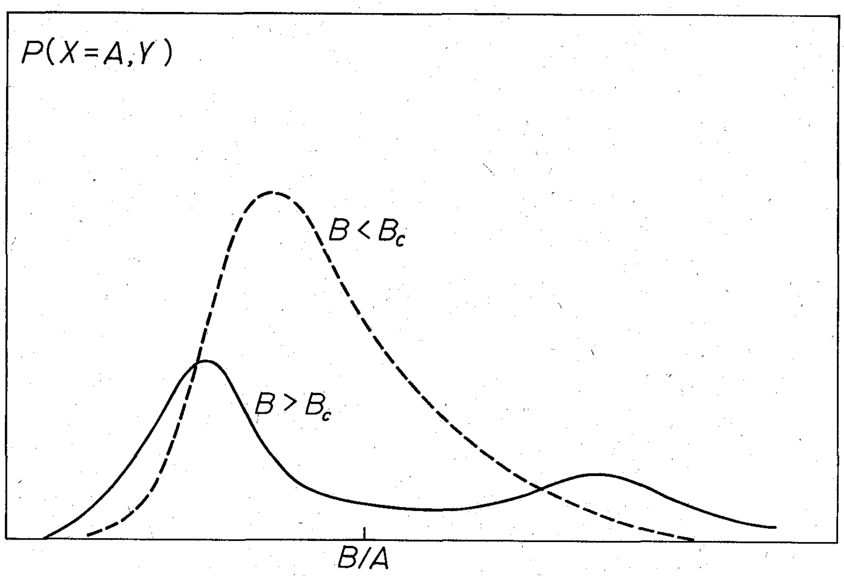

Fig. 4. Probability profile below and above the critical value B_c (not to scale).

Figure 5 represents the results of stochastic simulation of the time development of the autocorrelation function of the concentration of X.

We see the appearance of damped oscillations past the bifurcation point. Interestingly, as the size of the system increases a systematic component close to the phenomenological oscillation becomes more and more evident, with a correspondingly diminishing damping. It is tempting to conjecture that in the thermodynamic limit, $N \to \infty$, there would be an undamped oscillation indicating a high phase coherence in the form of a probability peak rotating along the limit cycle. This can be verified directly on the master equation by a calculation similar to that developed in the Appendix for the multiple steady-state model

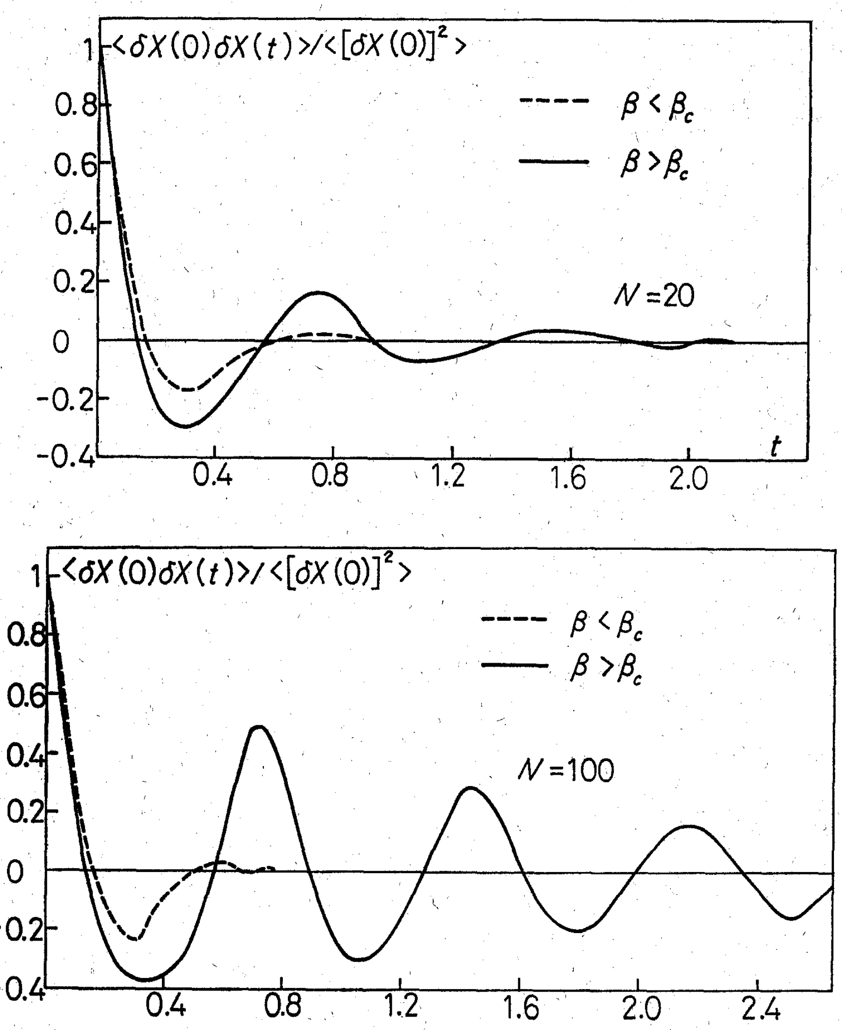

Fig. 5. Time dependence of normalized autocorrelation function characterizing the passage to a limit cycle. β=intensive bifurcation parameter; N=size parameter (in arbitrary units).

(see Eqs. (A·3), (A·4)).

There is of course no discrepancy between these results and the existence of a stationary probability crater found when the long-time limit $t \to \infty$ is taken before the thermodynamic limit. As in § 2, what is happening is that as N gets larger, the crater gets sharper, so that for $N \to \infty$ and $t \to \infty$ one gets:

$$P(\boldsymbol{\rho}) = \sum_{\phi} a(\phi)\,\delta\{\boldsymbol{\rho} - \bar{\boldsymbol{\rho}}(t;\phi)\}. \tag{3·2}$$

Here $\boldsymbol{\rho}$ denotes the couple $(X/N, Y/N)$, $\bar{\boldsymbol{\rho}}(t;\phi)$ is the phenomenological trajectory, ϕ denotes the phase along the periodic trajectory and $a(\phi)$ are appropriate weight coefficients. Note the analogy between Eq. (3·2) and the situation characterizing the ferromagnetic transition, and indeed, any transition associated with the breaking of a continuous symmetry group.

A reasonable Ansatz is that $a(\phi)$ is an increasing function of the mean sojourn times along the corresponding part of the limit cycle. This point is currently being investigated.[19]

§ 4. Effect of diffusion

In this section we consider again all-or-none transitions in systems involving a single fluctuating variable changing by jumps of ± 1 as in model (2·1). However, we are now interested in the effect of spatial fluctuations on the transition across the bifurcation point. We write the multivariate master equation in the more explicit form

$$\frac{P(\{X_\alpha\},t)}{dt}=\sum_{\alpha'}\{\lambda(X_{\alpha'}-1)P(\cdots,X_{\alpha'}-1,\cdots,t)-\lambda(X_{\alpha'})P(\{X_{\alpha'}\},t)$$
$$+\mu(X_{\alpha'}+1)P(\cdots,X_{\alpha'}+1,\cdots,t)-\mu(X_{\alpha'})P(\{X_{\alpha'}\},t)\}$$
$$+\text{diffusion}. \tag{4·1}$$

$\lambda(X_\alpha)$, $\mu(X_\alpha)$ represent the birth and death transition rates, respectively. For the Schlögl model, Eq. (2·1), they are given by

$$\lambda(X_\alpha)=\frac{3}{N}X_\alpha(X_\alpha-1)+(1+\delta')N\,,$$
$$\mu(X_\alpha)=N^{-2}X_\alpha(X_\alpha-1)(X_\alpha-2)+(3+\delta)X_\alpha\,. \tag{4·2}$$

Equation (4·1) can be solved exactly only in some particular cases, like the case of linear birth and death transition rates. Otherwise, one must appeal to approximations. One such approximation used widely recently[20)~22)] consists in truncation procedures or in Gaussian assumptions. Applying these techniques to the Schlögl model for a one-dimensional array of n cells with periodic boundary conditions, one finds that the space correlation of fluctuations around the steady state and for $\delta=\delta'\geqq 0$ is

$$\langle\delta X_\alpha\delta X_\beta\rangle=\langle X\rangle\delta^{Kr}_{\alpha,\beta}+\frac{8R}{d(R^2-1)(R^n-1)}(R^{|\alpha-\beta|}+R^{n-|\alpha-\beta|}),$$
$$|\alpha-\beta|=0,\ 1,\cdots,\ n-1 \tag{4·3a}$$

with

$$R=1+\frac{\delta}{d}+\left(\left(1+\frac{\delta}{d}\right)^2-1\right)^{1/2}. \tag{4·3b}$$

As $n\to\infty$ the range of correlations diverges as $|\delta|^{-1/2}$ when the bifurcation point $\delta=\delta'=0$ is approached. This is a classical law of divergence and leads to Eq. (2·6a) when integrated over the entire space.

We want now to go beyond this result. To this end, we condider again Eq. (4·1) and sum over all values of $X_{\alpha'}$, $\alpha' = \cdots, \alpha-1, \alpha+1, \cdots$. We then find, at the stationary state:

$$P(X_\alpha+1) = P(X_\alpha)\frac{\lambda(X_\alpha) + d/2\,(E(\alpha+1|X_\alpha)+E(\alpha-1|X_\alpha))}{\mu(X_\alpha+1)+d(X_\alpha+1)}, \quad (4\cdot 4a)$$

where

$$E(\xi|X_\alpha) = \sum_{X_\xi} X_\xi \frac{P(X_\xi, X_\alpha)}{P(X_\alpha)} \quad (4\cdot 4b)$$

represents the conditional average of X_ξ. A first approximation, developed some time ago by the authors[23] consists in adopting a "mean-field picture" whereby $E(\xi|X_\alpha)$ is independent of X_α. This is a reasonable assumption if the size of the cells is comparable to the correlation length. It leads to a nonlinear master equation for the one-cell probability $P(X_\alpha, t)$. We now extend this hypothesis by assuming that $E(\xi|X_\alpha)$ may depend on X_α and we limit ourselves to a linear dependence:[24]

$$E(\xi|X_\alpha) = \langle X_\xi\rangle + \frac{\langle \delta X_\xi \delta X_\alpha\rangle}{\langle(\delta X_\alpha)^2\rangle}(X_\alpha - \langle X_\alpha\rangle). \quad (4\cdot 5)$$

It can be shown that this relation is implied by the stronger assumption that the correlation function $G(X_\alpha, r_\alpha; X_\beta, r_\beta) = P(X_\alpha, r_\alpha; X_\beta, r_\beta) - P(X_\alpha, r_\alpha)P(X_\beta, r_\beta)$, where r denotes the cell position, can be factorized into a part depending on X_α and X_β only and a part depending on r_α and r_β. This is reminiscent of the approximation used in the well-known Enskog equation of the kinetic theory of dense gases.

Using Eqs. (4·3) and (4·1) one may find an expression for the space correlation function $\langle \delta X_\alpha \delta X_\beta\rangle$ at the steady state. For an infinite chain the result is:

$$\langle \delta X_\alpha \delta X_\beta\rangle = \langle X\rangle \delta^{Kr}_{\alpha,\beta} + \frac{ab}{d(a^2-1)} a^{-|\alpha-\beta|} \quad (4\cdot 6)$$

with

$$a = 1 + \frac{c}{d} + \left(\left(1+\frac{c}{d}\right)^2 - 1\right)^{1/2},$$

$$b = 2\langle X\rangle\left(\frac{\langle\lambda(X)\rangle}{\langle X\rangle} - c\right),$$

$$c = \frac{\langle X[\mu(X)-\lambda(X)]\rangle}{\langle(\delta X)^2\rangle}, \quad (4\cdot 7)$$

where the averages are taken over the one-cell probability distribution, Eq

(4·4a).

These expressions can be evaluated explicitly for the Schlögl model, Eq. (2·1). Numerical inspection suggests that c cannot vanish, whatever the value of δ, δ' (N being kept finite). Thus, the spatial correlations do not diverge at the bifurcation point $\delta=\delta'=0$. One cannot rule out of course a divergence in two or three dimensions. Work in this direction is in progress.

Independently of the predictions concerning the critical region around the bifurcation point, Eq. (4·6) has been tested away from the bifurcation point by a direct numerical simulation of the stochastic process of reactions and diffusion. The results are shown in Fig. 6 for $\delta=\delta'=0.01$. Also plotted is the result obtained from truncations, Eq. (4·3a). We see that the agreement between the simulations and the correction to the mean-field theory developed in this section is striking.

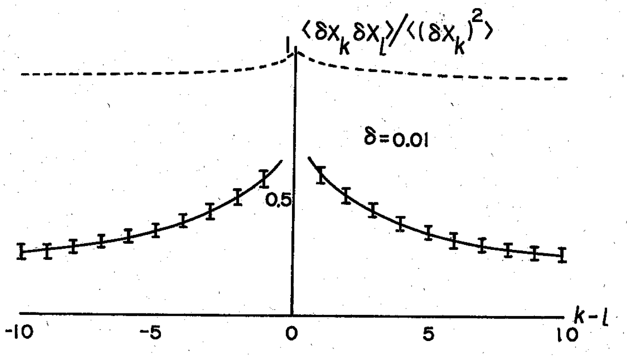

Fig. 6. Spatial correlation function for a periodic chain of 21 cells. Dashed curve represents the result obtained by the truncation of the hierarchy, Eq. (4·3a); solide curve that of the approximation (4·5).
Vertical bars represent the "computer experiments" result with 99% confidence intervals.

A different approach to spatially inhomogeneous fluctuations has been worked recently.[25),26)] The starting point is to incorporate the effect of fluctuations by an additive noise term $F(\boldsymbol{r},t)$ in the phenomenological rate laws, which then become stochastic differential equations. This term satisfies the usual condition $\langle F(\boldsymbol{r},t)\rangle=0$ and[27)]

$$\langle F(\boldsymbol{r},t)F(\boldsymbol{r}',t')\rangle=2\{\Gamma_1(\boldsymbol{r},\{X_i\},t)+D\nabla^2\Gamma_2(\boldsymbol{r},\{X_i\},t)\}\delta(\boldsymbol{r}-\boldsymbol{r}')\delta(t-t'), \tag{4·8}$$

where D is the diffusion coefficient matrix.

If Γ_1 and Γ_2 contain a constant term independent of the state variables, then Eq. (4·8) generates a theory which is completely equivalent to a time-dependent Ginzburg-Landau theory. On converting the stochastic differential equation to a Fokker-Planck equation one then finds a steady-state probability distribution provided a detailed balance condition holds. This is possible in systems involving a single fluctuating order parameter, like the systems treated in §2, or the Brusselator in the vicinity of bifurcation of spatially inhomogeneous steady-state solutions. The result is of the form

$$P \sim \exp \Psi , \tag{4·9}$$

where Ψ is the Landau-Ginzburg functional.[25] Hence, renormalization group methods[25),26] and scaling techniques[28] can be applied in the same way as in equilibrium critical phenomena. In systems undergoing all-or-none transitions and described by a cubic rate law (see Eqs. (2·1), (2·3a)), the theory is isomorphic to the Ising model. Hence, one finds a critical dimensionality of four and divergence of the variance and of the correlation length according to non-classical exponents below this dimensionality. On the other hand, in the Brusselator Ψ turns out to have a structure similar to that encountered in the analysis of anisotropic antiferromagnets, liquid crystals, and Rayleigh-Bénard instability. As a result, spatial fluctuations may destroy the bifurcation as well as the structures predicted by mean field theory in infinite one-and two-dimensional systems.

The connection between this formalism and the approach based on the multivariate master equation is a major open problem in fluctuation theory.

§5. Concluding remarks

The theory of fluctuations in chemical systems away from equilibrium leads to some fascinating problems of stochastic processes. Of special interest is the precise stochastic characterization of Hopf bifurcation, and the effect of diffusion at the level of a systematic perturbative treatment of the master equation in the vicinity of a bifurcation.

In addition to the internal fluctuations discussed throughout this paper there is a second mechanism of stochastic behavior, namely external noise. This arises from the fact that most of the systems of interest are subject to a complex environment that is itself fluctuating. Such fluctuations are modelled either as an additive noise (as in the Langevin picture briefly discussed in §4), or as a parametric effect entering into Eq. (1·1) through the fact that some of the parameters λ define a stochastic process. Under appropriate conditions on the noise one can convert then Eq. (1·1) into a Fokker-Planck equation of a type similar to Eq. (1·3). A systematic analysis of this equation has been undertaken recently.[29),30] The surprising result is that beyond a critical value of the variance, noise can introduce new transitions absent from the phenomenological rate laws, Eq. (1·1), or suppress transitions that would exist otherwise. An elegant experimental set up illustrating this behavior has been developed quite recently.[31] The entire field is still largely open and will undoubtedly undergo important developments in the next few years.

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Appendix

——*Perturbative Calculations in the Multiple Steady-State Region*——

We begin by transforming the master equation (2·4) to the generating function space:

$$f(s,t)=\sum_{X=0}^{\infty} s^X P(X,t), \quad |s|\leq 1. \tag{A·1}$$

We obtain

$$\frac{\partial f(s,\tau)}{\partial \tau}=(1-s)\left\{\frac{1}{N^2}s^2\frac{\partial^3 f}{\partial s^3}-\frac{3}{N}s^2\frac{\partial^2 f}{\partial s^2}+(3+\delta)\frac{\partial f}{\partial s}-(1+\delta')f\right\}. \tag{A·2}$$

We can check straightforwardly that in the limit $N\to\infty$ this equation is satisfied by the following family of solutions:

$$f(s,t)=e^{(s-1)(\bar{x}+1)/\varepsilon};\ \varepsilon=N^{-1}\ll 1, \tag{A·3}$$

where $\bar{x}$ satisfies the phenomenological equation (2·3a). Indeed, inserting into Eq. (A·2) we find:

$$e^{(s-1)(\bar{x}+1)/\varepsilon}\frac{d\bar{x}}{dt}=\{s^2(-(\bar{x}+1)^3+3(\bar{x}+1)^2)-(3+\delta)(\bar{x}+1)$$

$$+(1+\delta')\}e^{(s-1)(\bar{x}+1)/\varepsilon}.$$

If $|s-1|>0(\varepsilon)$, the above equation is satisfied identically in the limit $N\to\infty$ because of the negative exponential factor. Otherwise, the exponential factors cancel. Setting

$$s=1+\varepsilon\xi+\cdots,$$

we transform the remaining terms to

$$\frac{d\bar{x}}{dt}=-\bar{x}^3-\delta\bar{x}+(\delta'-\delta)+0(\varepsilon)$$

which is identical to (2·3a) in the thermodynamic limit. In other words, in this limit and for $t\to\infty$ the master equation is satisfied by functions sharply peaked (in fact: functions displaying a delta-function singularity) around the *stable* solutions of the phenomenological rate equation. This is in agreement with Kurtz's theorem, and suggests a systematic expansion of the master equation around (A·3)

$$f=f^{(0)}(1+\varepsilon^{\gamma}f^{(1)}+\varepsilon^{2\gamma}f^{(2)}+\cdots),$$
$$\gamma>0 \tag{A·4a}$$

together with

$$s=1+\varepsilon^{\theta}\xi_1+\varepsilon^{2\theta}\xi_2+\cdots,$$
$$\theta>0. \tag{A·4b}$$

Note that $f^{(0)}$ is singular in the thermodynamic limit. In this respect, Eqs. (A·4) bear strong resemblances with the ideas underlying singular perturbation theory.

Now, in a problem involving multiple steady states $f^{(0)}$ will be a sum of terms of the form (A·3), each centered on a stable attractor. The question is therefore how to assign weights to each of these terms without having to go through an explicit solution of the master equation.[32] For illustrative purposes we develop here a method for answering this question for the nonlinear Fokker-Planck equation corresponding to the master equation (2·4) or (A·2)

We first write Eq. (1·3) at the steady state in the form (setting $dP/dx=P'$, $d^2P/dx^2=P''$, etc$\cdots$):

$$\varepsilon P''+\frac{-2V(x)+\varepsilon D'(x)}{D(x)}P'+\frac{-2V'(x)+\varepsilon D''(x)}{D(x)}P=0. \tag{A·5}$$

It is easy to see that if $D(x)$ is positive, then for $\varepsilon=0$ this equation cannot admit a nonzero solution, unless $V(x)$ is vanishing at a certain set of points $\bar{x}$. This remark suggests that for $\varepsilon\neq0$ but small, P should be small everywhere except around the zeros of $V(x)$ where it will exhibit some kind of "resonance". The points $\bar{x}$ will then play the role of boundaries (see also comments at the end of § 2) around which we expect to have a "boundary layer" behavior. In order to explore their vicinity we follow a method developed by Matkowsky in the context of singular perturbations.[33] We set

$$P=A(x,\varepsilon)\exp\frac{2}{\varepsilon}\int^{x}\frac{V(\xi)}{D(\xi)}d\xi\equiv A(x,\varepsilon)\,e^{\mathcal{U}(x)/\varepsilon}, \tag{A·6}$$

where $\mathcal{U}(x)$ is the stochastic potential encountered in § 2. Note again the singular behavior of the exponential factor in ε in analogy to Eq. (A·3) of the first part of this appendix. Because of this, we seek for a (regular) perturbative expansion of $A(x,\varepsilon)$ in powers of ε:

$$A(x,\varepsilon)=\sum_n A_n(x)\,\varepsilon^n, \quad n\geq 0\,. \tag{A·7}$$

To zeroth order we obtain

$$\frac{V(x)}{D(x)}\left(A_0'+A_0\frac{D'}{D}\right)=0\,,$$

whose solution for any x different from $\bar{x}$ is:

$$A_0=C_0D^{-1}; \tag{A·8}$$

C_0 being an integration constant.

We now apply Eq. (A·6) to (A·8) in the vicinity of the resonance points $\bar{x}$ by expanding $V(x)$ around these points and keeping the first nontrivial terms. As in § 2, we assume that there exist two stable solutions $\bar{x}_+$, $\bar{x}_-$ of the phenomenological rate equation and an unstable solution at $\bar{x}_0=0$. We obtain in this way a global representation of P of the form:

$$\begin{aligned}P=&C_+\frac{D^{-1}(x)}{D^{-1}(\bar{x}_+)}\left(\frac{-2\varepsilon}{\mathcal{U}''(\bar{x}_+)}\right)^{-1/2}\exp\frac{1}{\varepsilon}\left\{\mathcal{U}(\bar{x}_+)+\frac{1}{2}\mathcal{U}''(\bar{x}_+)(x-\bar{x}_+)^2\right\}\\&+C_-\frac{D^{-1}(x)}{D^{-1}(\bar{x}_-)}\left(\frac{-2\varepsilon}{\mathcal{U}''(\bar{x}_-)}\right)^{-1/2}\exp\frac{1}{\varepsilon}\left\{\mathcal{U}(\bar{x}_-)+\frac{1}{2}\mathcal{U}''(\bar{x}_-)(x-\bar{x}_-)^2\right\}\end{aligned} \tag{A·9}$$

subject to the renormalization condition

$$C_++C_-=1\,. \tag{A·10}$$

If we require $\bar{x}_+$, $\bar{x}_-$ to coexist in macroscopic amounts, we must make sure that the ratio of the two probability peaks at $x=\bar{x}_+$ and $x=\bar{x}_-$ be of order unity. Because of the singular dependence of (A·9) in ε this yields

$$\mathcal{U}(\bar{x}_+)=\mathcal{U}(\bar{x}_-). \tag{A·11}$$

This is equivalent to the coexistence condition derived in § 2 from the exact solution of the master equation,[12] except of course that one has to adapt this condition to the Fokker-Planck equation.[13]

The next condition is that the two terms of (A·9) should match at $x=\bar{x}_0$. Consider the situation in the example of the Schlögl model. From § 2, $(\bar{x}_\pm-\bar{x}_0)^2=|\delta|$. Since $\mathcal{U}''(\bar{x}_\pm)$ is negative, the matching is automatically satisfied in the limit $\varepsilon\to 0$ as long as $|\delta|>0(\varepsilon)$. On the other hand, for $|\delta|<0(\varepsilon)$ (i.e., close to the bifurcation point $\delta=\delta'=0$) the exponentials in (A·9) tend to unity and the matching condition yields

$$\frac{C_+}{C_-}=\frac{D^{-1}(\bar{x}_+)\left(\frac{-2}{\mathcal{U}''(\bar{x}_+)}\right)^{1/2}}{D^{-1}(\bar{x}_-)\left(\frac{-2}{\mathcal{U}''(\bar{x}_-)}\right)^{1/2}}. \tag{A·12}$$

Again, this agrees with the results of the exact solution of the master equation[12] or of the nonlinear Fokker-Planck equation.[13] Thus, the weights of the probability peaks around the stable solutions can be calculated in a perturbative fashion.

The method is currently being extended[32] to a perturbative treatment of the time-dependent version of Eq. (A·5).

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Discussion

J. L. Lebowitz: What is the relation between the variables entering into the deterministic equation and the stochastic variables? Are the deterministic variables averages of the latter ones?

G. Nicolis: In simple situations, typically those described by single humped probability distributions, the phenomenological equations describing the evolution of the macrovariables are identical to the first moment equations of the master equation. In this case, the macrovariables are statistical averages of the stochastic variables. The situation may be different in the presence of simultaneously stable states. As we see in §2 of my talk, the first moment equation is no longer closed, since the variance of the fluctuations of extensive quantities is of the order of the square of the size of the system. Still, the phenomenological equations keep a meaning if the macrovariables are now interpreted as the most probable values, around which the probability peaks are centered.

N. G. van Kampen: What do you mean by "continuous Markov process"? The fact that x takes values in a continuous range does *not* imply that the nonlinear Fokker-Planck equation is valid.

G. Nicolis: You are right. One must also require that the two well-known Kolmogorov conditions on the transition probability be satisfied.

N. G. van Kampen: I do not think the macroscopic rate equations determine uniquely the transition probabilities that occur in the master equation.

G. Nicolis: To pursue the comment by Prof. van Kampen, one can say that in addition to the formal structure of the rate equations, one should specify that the various terms therein describe the rate of chemical reactions as given by the laws of thermodynamics and chemical kinetics. One has then a unique prescription for constructing the transition probabilities per unit time in the master equation.

J. Ross: What is the relation between $\mathcal{U}(x)$ and $\mathcal{V}(x)$?

G. Nicolis: The expression of the stochastic potential $\mathcal{U}(x)$ is complicated in the general case. Near the bifurcation point $\delta=\delta'=0$, however, it reduces to

$$-\mathcal{U}(x)=\frac{x^4}{4}-\frac{\delta'}{2}x^3+\frac{3\delta'-\delta}{4}x^2+(\delta-\delta')x,$$

where x is an intensive variable related to X by the first relation (2·2). Comparing with expression (2·3b) of the phenomenological potential $\mathcal{V}(x)$, we see that the major difference is the occurrence of the cubic term in $\mathcal{U}(x)$. This term compromises the validity of the Maxwell type rule and at the same time it introduces an asymmetry of $P(x)$ around the unstable state x_0.

P. C. Martin: I still have not understood. Do different methods give different predictions for the variances, for the existence of bifurcations, for the most probable states beyond bifurcations, or do all methods give the same answer? In the case of chemical processes, are you saying that in one dimension the fluctuations involving non-uniformities might wipe out the bifurcation as a one-dimensional phase transition is wiped out by fluctuations?

G. Nicolis: In §2, we have shown that the Kolmogorov equations (1·2) or (1·3) [neglecting the effect of diffusion] yield a coexistence condition beyond bifurcation which is different from the coexistence condition inferred from the Maxwell rule based on the phenomenological potential $\mathcal{V}(x)$ [Eq. (2·3a)]. The latter is also the condition that one would obtain using a Fokker-Planck equation with a constant diffusion coeffcient. Such an assumption is generally not justified for a chemical system. We conclude therefore that the coexistence condition based on Eq. (1·2) or (1·3) reflects better the dynamics of a chemical system. On the other hand, before bifurcation takes place these differences become irrelevant. Hence, the critical behavior of the variance [Eq. (2·6a)] is similar in all these approaches. The situation is much more complicated in the case of inhomogeneous fluctuations. In §4 we tried to explore some approaches like those based on the multivariate master equation and on the renormalization group ideas. The connection between them is, however, still an open problem. Experimental evidence is not yet available at this time.

H. Haken: In the discussion of metastable states and coexistence, one has to distinguish between systems described by space-independent (a) or space-dependent (b) variables. The probability distribution refers to an ensemble. Thus in case (a) at each time only a single (macroscopic) state is realized. In case of bistability, the symmetry is broken. The system may be driven by fluctuations from one state to another, but these states don't coexist. The situation is different in case (b) where at different space points different local states can be realized. But here the diffusion terms can lead to spatial (or temporal) patterns. One is then led to consider the realizability of the total pattern.

G. Nicolis: In the discussion of §2, "coexistence" is defined in terms of a stationary probability distribution and refers simply to the relative statistical weights of the stable states. In other words, if a large number of individual realizations of a stochastic processes take place starting with different initial conditions, we ask what the relative number of evolutions, which will be attracted to each of the stable states, will be. I believe that this sort of information is provided by the analysis of §2.

D. Walls: Are the asymptotic distributions in fact Poisson distributions which approach delta functions in the thermodynamic limit?

G. Nicolis: In the asymptotic evaluation of $P(x)$ [Eq. (2·7)], the delta functions [see Eq. (2·9)] appear as limits of Gaussian distribution functions as the size N goes to infinity. The Poisson distributions appear more naturally in the generating function representation used in the Appendix.