Information Contained in Open Systems by Example of Chemical Reaction Systems *

Ingo Decker
Institut A für Theoretische Physik der Technischen Universität Braunschweig,
D-3300 Braunschweig

Z. Naturforsch. **34a**, 915–943 (1979); received May 3, 1979

Spatially homogeneous chemical reaction systems with one or two intermediate reaction products and with autocatalytic reactionsteps are considered. Because of their non-linearities, such open systems show already primitive forms of self-organization. In order to express the "information" contained in the structures occuring, a theory is developped for measuring that quantity by help of a fictive detector: In treating the stochastic reaction kinetics in the Fokker-Planck-equation approximation, expressions are derived for the averaged amount of information one gets by doing a measurement with the detector and for the temporal conservation of the message being detected. This concept is applied to a one-component reaction scheme that exhibits a non-equilibrium phase transition of second order resulting in bistability of the steady state. When pushing this reaction system from the near equilibrium side through its critical region to bistability, a certain amount of information becomes quasi conserved, thus giving rise to a definition of the degree of order of a self-organizing system. The problem of how the reaction system can be integrated into a greater chemical network as a "bit"-generator, is discussed. To explain what is necessary for the onset of a hard mode instability giving birth to limit-cycle behaviour, a two-component reaction scheme is constructed by superposing onto reaction steps causing conservative concentration oscillations those reactions of the former model system which are responsible for the instability occuring there. By applying the information formalism, again, a quasi-conservation of information is indicated, but with respect to a much smaller time scale. The consequences for using oscillating reaction models as an information pump within a network, and the necessity of a feed-back mechanism in order to get real information storage, are shortly mentioned. Finally, a one-component reaction scheme is outlined that shows successive phase transitions, each of these instabilities bringing out a higher degree of organization.

Introduction

For describing phenomena of Nature, one has to distinguish between conservative and dissipative structures [1]. The former are directly induced by conservative interaction forces as is the case, e.g., for lattice structures of crystalline materials, the arrangement of atoms within macro-molecules of living matter, or the movement of our planetary system periodic in time. In principle, these structures are well understood by now. Dissipative structures [2, 3, 4, 5], however, which became subject to theoretical investigation only recently, appear, e.g., in chemical or biochemical reaction systems with autocatalytic or enzymatic reaction steps (anorganic Belusov-Zhaboutinsky reaction, temporal periodic concentration variation during the reduction process of sugar by glycolysis), but also in fields dealing with other things like cellular populations (formation of a plasmodium by slime molds) or hydrodynamic transport phenomena (Bénard problem). These structures can be defined as states organized in space, in time, or in space and time, which come into being within open systems only far away from thermodynamic equilibrium and which are maintained by permanent dissipation of energy. More exactly, these structures are separated from thermal equilibrium by a discontinuity, i.e., by a kinetic (non-equilibrium) phase transition [6, 7].

Apparently, there seems to be a contradiction between the second law of thermodynamics — which, because of its statement of irreversibly increasing entropy, is looked upon as a law of decreasing organization, i.e., of vanishing structure originally fixed by some initial conditions — and the fact of increasing organization, i.e., the production of more and more complex structures by the evolution process [8]. The theory of dissipative structures can help to close this gap of understanding. Although the macroscopic spatial structures predicted should not be the key for the formation of functional order in evolution of life, it rather is the underlying mechanism of non-equilibrium thermodynamics that is essential and that has to be

---

* This work was partially supported by a fellowship of the Max-Planck-Gesellschaft (MPI für Biophysikalische Chemie, Göttingen-Nikolausberg).

Reprint request to Herrn I. Decker, Institut A für Theoretische Physik, Technische Universität Braunschweig, D-3300 Braunschweig.

0340-4811 / 79 / 0800-0915 $ 01.00/0

translated from the real (geometrical) space into a language based on coordinates which already incorporate the functions of macromolecular structures such as nucleic acids and proteins [9].

In this framework, the notion "information" is of central meaning because it is just a quantity that can be interpreted as an integral form of the highly complex real space structures within living matter and of their functional aspects. But if we want to bring the evolution process into a strictly mathematical formulation, we meet with the following difficulty: In the field of self-organization, not the amount but rather the value of information is important [10, 9, 1], whereas the mathematical information measure developped in communication theory is only dedicated to syntactic (the amount), but not to the semantic or pragmatic aspects of "information" [11, 12]. Till now, a description including the value of information was only possible in some special situations [13] as, e.g., in the selection model proposed by Eigen [9].

It is not the aim of this paper to go deeper into the biological problems quoted above. We return to open systems that are as simple as to show first steps of self-organization of matter, and we intend to contact information theory not only to the statics (i.e., the steady state behaviour) of open systems, but also to the dynamic properties, as closely as possible. For this purpose, we exclusively deal with common mathematical theory of information and we will see how the increase of the amount of information is correlated to non-equilibrium phase transitions [14]. On the other hand, also here, the question about the "value" of information automatically comes out when the open system is treated as an element of a network of open systems. However, we will be able to answer this problem in a quite natural way (cf. Section V.4).

In order to have some concrete model systems for discussing information containment in open systems, we deal with chemical reaction systems including autocatalytic reaction steps. Their disposition is assumed to be of the following kind: The concentrations $a, b, \dots$ of the initial substances $A, B, \dots$ and the concentrations $e, f, \dots$ of the final products of the reaction, $E, F, \dots$ are stabilized from outside at constant values throughout the whole reaction volume. The concentrations $x, y, \dots$ of the intermediate molecules $X, Y, \dots$, however, move freely due to the reaction kinetics. Here, we restrict ourselves to systems with only one or two degrees of freedom (i.e., with one or two intermediates) which are characterized by fast diffusion processes and thus can be treated as spatially homogeneous reaction systems. Consequently, we only have to speak about non-equilibrium phase transitions giving birth to multistable steady states and to dissipative structures organized in time (i.e., to limit cycles).

It is the author's intention to make this paper self-contained and to keep it legible to a wider group of readers. Therefore, facts about information theory, reaction kinetics, stochastics, and phase transition phenomena, already well known, are reviewed to an extent as just is necessary. It is tried to put together these disciplines, and to make further development, in a transparent manner, using a mathematical formulation as simple as possible. This paper aims to present the problem of self-organization in a unified "information picture", hoping that this framework can help a little to find out a more general information concept capable of including functional aspects.

I. Mathematical Definition of Information

Before going into discussion of information containment in chemical reaction systems we should place together the basic concepts of information theory [11, 15].

I.1. The Classical Information Concept

We consider a system called S_N which is characterized by a set of N microstates φ_i, $i = 1, \dots, N$. To begin with, we assume to have no knowledge about the actual state of the system except that it will be in one of the possible microstates at any definite time. Then, the information we will get by a measurement testing the actual state of S_N is given by [16]

$$J(N) = \mathrm{ld}\, N \tag{1}$$

(with $\mathrm{ld}\, N =_{\mathrm{def}} \log_2 N$ so that the unit of J is just one "bit"!). This information measure has the following properties:

i) $J(n)$ is a positive definite function monotonously increasing with the number n of possible microstates.

ii) $J(n)|_{n=1} = 0$: If we know that S_N can stay at only one of the φ_i, a following measurement will give us no further information.

iii) $J(n)$ is an additive (extensive) quantity: If we take a second system S_M with M microstates φ_k in addition to S_N without S_N and S_M coming into interaction, the combined system $S_N \times S_M$ possesses $M \cdot N$ microstates (φ_i, φ_k). Then, a measurement determining the actual state of $S_N \times S_M$ gives the information

$$J(N \cdot M) = \operatorname{ld} N \cdot M = J(N) + J(M).$$

In most cases we have somewhat more prior knowledge about the system, namely, e.g., that S_N prefers some of the φ_i while the other states are realized with a minor probability. Describing that by a probability distribution $P_N = (p_1, p_2, \ldots, p_N)$ where p_i is just the probability for finding S_N in state φ_i (with normalization $\sum_{i=1}^{N} p_i = 1!$), we may ask for the amount of additional information we now get by measurement. Averaging over all possible events of the measurement, that information is given by [17, 18].

$$J(P_N) = -\sum_{i=1}^{N} p_i \operatorname{ld} p_i . \tag{2}$$

This expression is smaller than $J(N)$. Only when P_N approaches equipartition, i.e. $p_i \equiv N^{-1}$ for all i, $J(P_N)$ reaches its maximum and becomes equal to $J(N)$. Thus, the quantity

$$K^*(P_N) =_{\text{def}} J(N) - J(P_N) = \sum_{i=1}^{N} p_i \operatorname{ld} (p_i \cdot N) \tag{3}$$

can be regarded as an information measure for knowing the distribution P_N.

It should be remarked that there is a close connection between "information" and the entropy in statistical mechanics [4, 19]. But here we omit a detailed discussion because it is of no use in the context of this paper.

I.2. The Concept of Information Gain

Till now, we implied that there exists a detector being able to perceive exactly the momentary microstate of S_N. In the case of chemical reaction systems treated here, however, this requirement surely is not fulfilled: The microstates are labeled each by a fixed number of the intermediate molecules within the reaction volume. This number fluctuates very rapidly so that any realistic detector can only give the mean value of that number with respect to the time interval necessary for the measurement, or, perhaps, the mean square of the corresponding fluctuations, i.e., we get the first moments of a frequency distribution $P_{N,\text{detect}}$.

In order to express the gain of information we get with regard to our prior knowledge of P_N when detecting $P_{N,\text{detect}}$, it is not ingenious to determine this quantity $K(P_{N,\text{detect}}/P_N)$ simply by the difference between $J(P_{N,\text{detect}})$ and $J(P_N)$: for instance, if we assume $P_{N,\text{detect}}$ and P_N to be distributions of the same shape, but separated from each other — e.g., $p_{i,\text{detect}} = p_{(N/2+)i} = 0$ for $i = 1, \ldots, N/2$ and $p_{i,\text{detect}} = p_{i-(N/2)} \neq 0$ for $i = (N/2)+1, \ldots, N$ — the difference

$$J(P_{N,\text{detect}}) - J(P_N)$$

is zero, i.e., a detection of a distribution highly improbable with respect to P_N would give us no information. That, however, is of no sense in the framework of information theory. For the definition of $K(P_{N,\text{detect}}/P_N)$, we can argue in the following way: The uncertainty of the event of "S_N being in φ_i" is given by $-\operatorname{ld} p_i$ before measurement and by $-\operatorname{ld} p_{i,\text{detect}}$ afterwards. By averaging $(-\operatorname{ld} p_{i,\text{detect}}) - (-\operatorname{ld} p_i)$ over $P_{N,\text{detect}}$, we get a quantity for the loss of uncertainty during the measurement, or, as the complementary (sign-reversed) quantity, the information gain [20, 4]

$$K(P_{N,\text{detect}}/P_N) = \sum_{i=1}^{N} p_{i,\text{detect}} \operatorname{ld} \frac{p_{i,\text{detect}}}{p_i} . \tag{4}$$

This functional — which is equal to $K^*(P_{N,\text{detect}})$ of Eq. (3) in the equipartition case $p_i = N^{-1}$ — has only positive values and becomes zero only if $P_{N,\text{detect}}$ and P_N are identical distributions.

As in relation (2), we also here want to have an information measure that is independent of actual results of a measurement. Therefore, we have to consider all possible detector outputs $P_{N,\text{detect}}(j)$ and to average over all corresponding information gains, $K(P_{N,\text{detect}}(j)/P_N)$, by use of probabilities $p_{\text{d}}(j)$ for the distributions $P_{N,\text{detect}}(j)$ occuring as output,

$$J(\alpha/P_N) = \sum_{j} p_{\text{d}}(j)\, K(P_{N,\text{detect}}(j)/P_N) . \tag{5}$$

Here, α stands for the set of characteristic detector parameters. An example of how to define and calculate the $P_{N,\text{detect}}(j)$'s and the $p_{\text{d}}(j)$'s as functions of α and the dynamic properties of the reaction system, will be shown in the next section.

For this problem, at this stage, we only remark that, if the detector is an ideal one (is able to indicate single microstates), the distributions $P_{N,\,\mathrm{detect}}(j)$ become equal to the Kronecker Delta $\delta_{i,j}$ and the $p_{\mathrm{d}}(j)$ are given by p_j. Inserting this into Eq. (5), the expression $J(\text{"ideal"}/P_N)$ becomes, as it should be, identical to $J(P_N)$ of Equation (2).

In the case of macroscopic systems, the number of microstates (here: the maximal number of molecules within the reaction volume) is very large ($\sim 10^{22}$) and thus, in order to simplify the mathematical procedure, it is allowed to replace the discrete index i by the continuous variable x (here denoting the concentrations of the intermediate substances) and the probability distributions P_N by density functions $\varrho(x)$. Limiting x to the interval $0 \leqq x \leqq 1$, we have $x_i = i \cdot N^{-1}$ ($\Delta x = N^{-1}$!) and, because of the normalization that has to be required also for $\varrho(x)$:

$$\int_0^1 \varrho(x)\,\mathrm{d}x = 1 \quad \Big(\overset{!}{=} \sum_{i=1}^{N} p_i\Big),$$

$$\varrho(x_i) = \lim_{N\to\infty} N \cdot p_i\,.$$

In contrast to the information measure $J(P_N)$, there is no difficulty to transform the expression for the information gain into the language of continuous functions:

$$\lim_{N\to\infty} K(P_{N,\,\mathrm{detect}}/P_N) = \int_0^1 \varrho_{\mathrm{detect}}(x)\,\mathrm{ld}\,\frac{\varrho_{\mathrm{detect}}(x)}{\varrho(x)}\,\mathrm{d}x$$
$$= K(\varrho_{\mathrm{detect}}/\varrho)\,. \tag{6}$$

Regarding that there may be also a "continuum" of possible detector outputs $\varrho_{\mathrm{detect}}(x/z)$, the continuous version of the quantity $J(\alpha/P_N)$,

$$J(\alpha/\varrho) = \int_{-\infty}^{+\infty} \varrho_{\mathrm{d}}(z)\,K(\varrho_{\mathrm{detect}}(z)/\varrho)\,\mathrm{d}z\,, \tag{7}$$

then yields an information measure which is primarely dependent on the kind of the detector and, as we will see in the next chapter, on the kinetics of the system considered, but which is no longer a direct function of the system size, as it is the case for $J(P_N)$.

II. Relating Information Theory to Chemical Reaction Systems

In order to explain the procedure to be employed in the following chapters in some detail without any avoidable mathematical complication, we start with the simplest reaction scheme [3] being possible within the framework outlined in the introduction:

$$A \underset{k_{\leftarrow}^{(1)}}{\overset{k_{\rightarrow}^{(1)}}{\rightleftharpoons}} X\,, \qquad X \underset{k_{\leftarrow}^{(2)}}{\overset{k_{\rightarrow}^{(2)}}{\rightleftharpoons}} E\,; \tag{8}$$

i.e., the molecules of the initial substance A may be transformed into X-molecules by help of a catalyser, and then, induced by another catalyser, the intermediate X- may change into the final E-substance. In the framework of deterministic reaction kinetics [21, 5], the concentration of the X-substance within the reaction volume obeys the rate equation

$$\frac{\mathrm{d}}{\mathrm{d}t}\,x = R_{+X} - R_{-X} =_{\mathrm{Def}} v(x)\,, \tag{9}$$

and the rates for increase and decrease of the number of X-molecules are given by

$$R_{+X} = k_{\rightarrow}^{(1)}\,a + k_{\leftarrow}^{(2)}\,e\,, \tag{10a}$$
$$R_{-X} = (k_{\leftarrow}^{(1)} + k_{\rightarrow}^{(2)})\,x\,. \tag{10b}$$

For externally fixed a, b, $v(x)$ has one zero point, $x = x_0$. Because of $v(x) > 0$ for $x < x_0$ and $v(x) < 0$ for $x > x_0$, the concentration x_0 denotes a stable stationary solution of Eq. (9) — called the steady state — that the reaction system will approach when the time t goes to infinity, irrespective of the initial value of the X-concentration, $x(t_0)$.

II.1. Master-equation Approach

Now, it is our task to introduce concentration fluctuations by a stochastic treatment. We will do this by help of the so called "birth and death process" [22, 3, 4, 23, 30]. For this purpose, instead of the continuous variable x, we return to the number of X-molecules within the reaction volume, n_X, and denote the probability of finding just n_X molecules at time t by $p(n_X; t)$. The time-development of the system is determined by

$$p(n_X; t+\tau) = \Bigg(1 - \sum_{\substack{n=0\\ n\neq n_X}}^{N_x} W_{n_X\to n}(\tau)\Bigg)\, p(n_X; t) \tag{11}$$
$$+ \sum_{\substack{n=0\\ n\neq n_X}}^{N_X} W_{n\to n_X}(\tau)\, p(n; t)\,,$$

where the $W_{n\to n'}(\tau)$ are the conditional probabilities that the system is in state "n'" after the time interval τ if it was in state "n" at time t. (N_X: number of X-molecules when the reaction volume V

is filled only by the X-substance; for convenience, we introduce a length scale so that $N_X = V$.)

The transition probabilities $W_{n \to n'}(\tau)$ can be related to the reaction kinetics in the following way: For small τ, the probability that the reaction system (8) produces one new X-molecule during τ ("birth") is given by $VR_{+X}\tau$, while the destruction of one X-molecule ("death") is of probability $VR_{-X}\tau$. Due to the factorization of the joint probability in the case of a set of statistically independent events, the probability for creation {annihilation} of ν molecules can be approximated by $V(R_{+X}\tau)^\nu \{V(R_{-X}\tau)^\nu\}$. Inserting this into Eq. (11) and taking the limit $\tau \to 0$, we get the master equation

$$\begin{aligned}\frac{\partial}{\partial t} p(n_X;t) = &- V(R_{+X} + R_{-X})|_{x=n_X/V} \cdot p(n_X;t) \\ &+ V(R_{-X}|_{x=(n_X+1)/V} \cdot p(n_X+1;t) \\ &+ R_{+X}|_{x=(n_X-1)/V} \cdot p(n_X-1;t)), \quad (12)\end{aligned}$$

i.e., here, only the probabilities for microstates being directly in neighbourhood to each other are dynamically coupled. Because of the coefficients of this master equation being independent of time and of the actual distribution $p(n;t)$, Eq. (12) determines a stationary Markovian process [24, 4].

II.2. Stationary Solution and the Property of Decreasing Mixing Distance

The solution $p(n_X;t)$ of a stationary Markovian process tends to a stationary limiting distribution

$$\lim_{t\to\infty} p(n_X;t) = p_\infty(n_X) . \quad (13)$$

In the case considered here, this distribution can be calculated in a totally algebraic manner by using the principle of detailed balance [25, 4]

$$W_{(n_X-1)\to n_X}\, p_\infty(n_X-1) = W_{n_X\to(n_X-1)}\, p_\infty(n_X) . \quad (14)$$

Because of

$$W_{(n_X-1)\to n_X} : W_{n_X\to(n_X-1)} = R_{+X}|_{x=(n_X-1)/V} : R_{-X}|_{x=n_X/V} = \mu/n_X ,$$

this yields a Poissonian distribution

$$p_\infty(n_X) = C\,\frac{\mu^{n_X}}{n_X!} , \quad (15)$$

where C is a constant preserving the normalization of $p_\infty(n_X)$. (In the case of reaction systems with more than one intermediate substance (cf. Chap. V), detailed balance is no longer guaranteed [26] so that other procedures are necessary for evaluating the stationary solution $p_\infty(n_X)$ [27].)

In order to characterize the dynamical behaviour, the quantity

$$K = \sum_{n_X=0}^{V} p(n_X;t) \ln (p(n_X;t)/p_\infty(n_X)) \quad (16)$$

has been introduced [28]. For every stationary Markovian process, this K-functional which has the mathematical meaning of information gain (see Chap. I!), decreases monotonously when time is going on. (For that reason, the K-functional has been proposed as a basis for determining the entropy in open systems far away from thermal equilibrium.) A more stringent characterization of the Markovian property we get by the statement that all the functionals

$$J[G] = \sum_{n_X=0}^{V} p_\infty(n_X)\, G(p(n_X;t)/p_\infty(n_X)) , \quad (17)$$

with any arbitrary convex function $G(u)$ — and not only the "negative entropy" K where $G = u \cdot \ln u$ — decrease monotonously with time t. This property is called the principle of decreasing mixing distance [29, 31].

II.3. Reduction to a Fokker-Planck Equation

For the sake of simplicity of the mathematics, we return to a continuous description again: $n_X V^{-1} \to x$, $V p(n_X;t) \to \varrho(x;t)$. Inserting this into Eq. (12) and expanding the functions $R_{\pm X}(x \pm 1/V)$ and $\varrho(x \pm 1/V;t)$ up to terms linear and, respectively, quadratic in the deviation $\pm 1/V$, we arrive at the Fokker-Planck equation

$$\frac{\partial}{\partial t}\varrho(x;t) = -\frac{\partial}{\partial x}\{v(x)\,\varrho(x;t)\} + \frac{1}{V}\frac{\partial^2}{\partial x^2}\{D(x)\,\varrho(x;t)\} \quad (18)$$

with

$$D(x) = \tfrac{1}{2}(R_{+X} + R_{-X}) .$$

Our motivation for doing this expansion is based on the requirement that the approximation shall be as good as to result in a Gaussian distribution in the case of normal fluctuations [3, 26, 30, 32]. In this case, the concentration fluctuations scale as

$$x - \langle x(t)\rangle = \sqrt{1/V}\,\xi$$

where the mean square fluctuation of ξ, $\langle\xi^2\rangle$, is of the order of unity [33]. ($\langle x(t)\rangle$ denotes the mean value $\int_0^1 x\,\varrho(x;t)\,\mathrm{d}x$, and for the definition of $\langle\xi^2\rangle$ see Equation (22).) Introducing the ξ-coordinate into Equation (18):

$$\varrho(x;t) \to \sqrt{V}\,\Phi(\xi;t)\,,$$

in leading order of V, we get

$$\frac{\partial}{\partial t}\langle x(t)\rangle\left[\frac{\partial}{\partial\xi}\Phi(\xi;t)\right] = v(\langle x(t)\rangle) \cdot\left[\frac{\partial}{\partial\xi}\Phi(\xi;t)\right]. \tag{19}$$

Thus, the dynamical behaviour of the mean value can be separated and is governed by a law identical to the rate equation of deterministic reaction kinetics. To next (smaller) order of V, there appears a modified Fokker-Planck equation

$$\frac{\partial}{\partial t}\Phi(\xi;t) = -\left.\frac{\partial}{\partial x}v(x)\right|_{x=\langle x(t)\rangle}\frac{\partial}{\partial\xi}\{\xi\,\Phi(\xi;t)\} + D(\langle x(t)\rangle)\frac{\partial^2}{\partial\xi^2}\Phi(\xi;t)\,, \tag{20}$$

which, indeed, has a Gaussian distribution as its solution

$$\Phi(\xi;t) = \frac{1}{\sqrt{2\pi}}\frac{1}{\sqrt{\sigma(t)}}\exp\left(-\frac{\xi^2}{2\,\sigma(t)}\right). \tag{21}$$

The time development of the corresponding mean square fluctuation

$$\sigma(t) \equiv \langle\xi^2\rangle = \int_{-\infty}^{+\infty}\xi^2\,\Phi(\xi;t)\,\mathrm{d}\xi$$

is determined by

$$\frac{\partial}{\partial t}\sigma(t) = 2\left.\left\{\frac{\partial}{\partial x}v(x)\,\sigma(t) + D(x)\right\}\right|_{x=\langle x(t)\rangle}. \tag{22}$$

This system size expansion just outlined is only valid if the variance of the fluctuation distribution, $\sigma(t)$, remains much smaller than of order V during all the time ($\langle\xi^2\rangle \sim O(1)$!). For the reaction system of Eq. (8), the derivative $\frac{\partial}{\partial x}v(x)$ is a constant of negative value and, hence, the differential equation (22) keeps $\sigma(t)$ bounded so that the system size expansion is applicable. Together with

$$\lim_{t\to\infty}\langle x(t)\rangle = x_0\,,$$

$\sigma(t)$ approaches the limiting value

$$\lim_{t\to\infty}\sigma(t) = \left.\frac{D(x)}{\left|\frac{\partial}{\partial x}v(x)\right|}\right|_{x=x_0} = \sigma_\infty\,. \tag{23}$$

Therefore, the stationary solution of the Fokker-Planck equation, as a function of the concentration x, is given by

$$\varrho_\infty(x) = \frac{1}{\sqrt{2\pi}}\frac{1}{\sqrt{V^{-1}\sigma_\infty}}\exp\left(-\frac{(x-x_0)^2}{2\,V^{-1}\sigma_\infty}\right). \tag{24}$$

Comparing this result to the exact limiting distribution of the initial master equation, we find the first and the second moment of that Poissonian distribution, μV^{-1} and μV^{-2} (resulting from Eq. (15) if the X-concentration is introduced there!) in fact identical to those of $\varrho_\infty(x)$, x_0 and $V^{-1}\sigma_\infty$. The deviations of the higher moments, however, are due to the approximation of the master equation by a Fokker-Planck equation.

For chemical reaction systems showing non-equilibrium phase transitions, as to be discussed in the following sections, the concentration fluctuations become large when the system approaches its phase transition point [30], i.e., in terminology of the system size expansion, because of

$$\left.\frac{\partial}{\partial x}v(x)\right|_{x=\langle x(t)\rangle} \to 0\,,$$

Eq. (22) would induce the variance, $\sigma(t)$, to diverge at that critical point. In this case we must go back to the full Fokker-Planck equation (18) and try to get differential equations for the moments of the fluctuation distribution without postulating a scaling behaviour of the fluctuations. (That Eq. (18) should be a good approximation also in these critical regimes, can be argued as follows: With increasing $\sigma(t)$, $\varrho(x;t)$ smooths down more and more so that the second-derivative term of Eq. (18) — and this term was already sufficient for the strongly peaked $\varrho(x;t)$-curvature in the normal fluctuation case — becomes less important compared to the first-derivative terms.) From Eq. (18) and by repeated partial integration, we get

$$\frac{\partial}{\partial t}\langle x^\nu\rangle = \int_0^1 x^\nu\frac{\partial}{\partial t}\varrho(x;t)\,\mathrm{d}x = \nu\,\langle x^{\nu-1}\,v(x)\rangle + \frac{1}{V}\nu(\nu-1)\,\langle x^{\nu-2}\,D(x)\rangle. \tag{25}$$

Expanding the functions $v(x)$ and $D(x)$ by the power series

$$v(x)=\sum_{n=0}^{\infty} v_n\, x^n\,, \quad D(x)=\sum_{n=0}^{\infty} d_n\, x^n\,,$$

and taking account of the connection between the mean value of the ν-th x-power and the moments of $\varrho(x;t)$,

$$\langle x^\nu\rangle=\sum_{i=0}^{\nu}\binom{\nu}{i}\langle x\rangle^{\nu-i}\langle(x-\langle x\rangle)^i\rangle\,, \tag{26}$$

we arrive at a hierarchy of differential equations connecting the moments of $\varrho(x;t)$ to each other. Since this hierarchy is based on the Fokker-Planck approximation of Eq. (18) (and not on the exact master equation [3]), for the purpose of a consistent calculation, we have to "close" this hierarchy with respect to the lowest moments by approximating the higher moments as functions of the lower ones in the Fokker-Planck sense. How this can be done in the case of a concrete reaction system, will be shown in the following chapters. Here, we only should note: If we use $v(x)$ of the reaction system (8) and approximate $D(x)$ by the constant value $D(\langle x\rangle)$, the differential equations for the first and the second moment decouple from the rest of the hierarchy and become, as it should be, identical to the Eqs. (19) and (22).

Finally, like the K-functional cited in Eq. (16), also the corresponding functional

$$K(\varrho(t)/\varrho_\infty)=\int_0^1 \varrho(x;t)\ln\frac{\varrho(x;t)}{\varrho_\infty(x)}\,\mathrm{d}x \tag{27}$$

decreases monotonously with time t, if $\varrho(x;t)$ is governed by a Fokker-Planck equation and $\varrho_\infty(x)$ is its limiting distribution [34].

II.4. Definition of the Information Measure

After we have roughly collected the basic features of the stochastics of a chemical reaction system, we are now able to get contact with the formulae of information theory outlined in Chapter I. In its continuous version, the probability distribution P_N introduced there (that comprises the prior knowledge about the system) is most reasonably identified with the limiting distribution, $\varrho_\infty(x)$, of the Markovian process, because only $\varrho_\infty(x)$ is uniquely defined by the boundary conditions (concentrations of the initial and final substances, temperature), the kind of the reaction procedure (parametrized by the reaction constants $k_{\rightleftarrows}^{(\nu)}$) and the nature of the stochastic process.

In order to express possible detector outputs $\varrho_{\text{detect}}(x/z)$, we assume the detector to be almost ideal in that sense that it needs some time interval τ for the measurement, but has the ability of a total resolution within the x-coordinate. If the concentration of the X-molecules is exactly given by $x(t_0)=z$ at the time $t=t_0$, during the interval $t_0<t<t_0+\tau$, the detector then records the frequency distribution

$$\varrho_{\text{detect}}(x/z)=\frac{1}{\tau}\int_{t_0}^{t_0+\tau}\tilde{\varrho}(x;t)\,\mathrm{d}t \tag{28}$$

with the "integrand" being fixed by the initial condition $\tilde{\varrho}(x,t_0)=\delta(x-z)$ and the time dependence of $\tilde{\varrho}(x,t)$ being developped by the reaction stochastics. On the other hand, the probability of getting just that "output," $\varrho_{\mathrm{d}}(z)$, is equal to $\varrho_\infty(z)$, because $\varrho_\infty(x)\,|_{x=z}$ is the probability distribution for finding the system at $x=z$ at time t_0, if we assume the concentration fluctuations to be in their stationary regime so that they have already become independent of the initial preparation of the reaction system.

This definition of the probability distribution $\varrho_{\mathrm{d}}(z)$ corresponds to the experimental situation that we repeat the detector measurement again and again in the course of time, receiving a series of detector outputs, $\varrho_{\text{detect}}(x/\nu)$, $\nu=1,2,\ldots$. If the reaction system was prepared at time $t=0$ with the initial X-concentration $x=x(0)$, according to the stochastic reaction kinetics, the x-values at later times become random numbers governed by a probability distribution $\tilde{\tilde{\varrho}}(x;t)$ which obeys the initial condition $\tilde{\tilde{\varrho}}(x,0)=\delta(x-x(0))$. Therefore, the probability density that the ν-th detector output $\varrho_{\text{detect}}(x/\nu)$ measured within the time interval $t_{0,\nu}<t<t_{0,\nu}+\tau$ is identical to $\varrho_{\text{detect}}(x/z)$ of Eq. (28), is given by $\tilde{\tilde{\varrho}}(z;t_{0,\nu})$. Averaging over all detector measurements, the probability of finding the output $\varrho_{\text{detect}}(x/z)$ is given by

$$\varrho_{\mathrm{d}}(z)=\lim_{\nu_{\max}\to\infty}\frac{1}{\nu_{\max}}\sum_{\nu=1}^{\nu_{\max}}\tilde{\tilde{\varrho}}(z,t_{0,\nu})\overset{!}{=}\varrho_\infty(z)$$

and, hence, is indeed independent of the initial preparation of the reaction system. The reason is that $\tilde{\tilde{\varrho}}(x;t)$ tends to the limiting distribution $\varrho_\infty(x)$ irrespective of its initial form (this is guaranteed by the Markovian character of the stochastic process) and, in the summation of the above relation, the terms of $\tilde{\tilde{\varrho}}(x;t)$ deviating from $\varrho_\infty(x)$ are dominated by the $\varrho_\infty(x)$-terms in the $(\nu_{\max} \to \infty)$-limit.

Because of the difficulties of a general analytic evaluation of Eq. (28), in all that follows, we roughly approximate the integral by $\tau \cdot \tilde{\varrho}(x; t_0 + \tau/2)$,

$$\varrho_{\text{detect}}(x/z) \cong \tilde{\varrho}(x; t_0 + \tau/2) \quad \text{with} \quad \tilde{\varrho}(x; t_0) = \delta(x - z)\,. \tag{28a}$$

In the case of the reaction scheme (8), from Eqs. (19), (22) and by using the initial conditions $\langle x(t_0)\rangle = z$, $\sigma(t_0) = 0$ and setting approximately $D(x) \equiv D(x_0)$, we get for the time dependence of the first and the second moment of $\tilde{\varrho}(x;t)$ and, hence, for those of $\varrho_{\text{detect}}(x/z)$ when $t = t_0 + \tau/2$,

$$\langle x(t)\rangle = x_0 + (z - x_0)\exp(-|v_1|(t - t_0))\,, \tag{29a}$$

$$\sigma(t) = \sigma_\infty\{1 - \exp(-2|v_1|(t - t_0))\}\,, \tag{29b}$$

with $v_1 = \dfrac{\partial}{\partial x} v(x)$. Inserting the corresponding Gaussian form of $\varrho_{\text{detect}}(x/z)$ and the solution (24) of $\varrho_\infty(x)$ into Eq. (7) ($\varrho_{\text{d}}(t) \equiv \varrho_\infty(z)$!), the quantity $J(\alpha = \tau/\varrho = \varrho_\infty)$ amounts to

$$J(\tau/\varrho_\infty) = -\tfrac{1}{2}\,\text{ld}\{1 - \exp(-|v_1|\,\tau)\} = \tfrac{1}{2}\,\text{ld}\left(\frac{1}{|v_1|\,\tau}\right), \tag{30}$$

where the second part is obtained by expanding the exponential for small τ. Here, we find the reaction constant combination $|v_1| = k_{\leftarrow}^{(1)} + k_{\rightarrow}^{(2)}$ as the only parameter of the reaction system that enters the information measure chosen here. For the $|v_1|$ as well as the τ-dependence of $J(\tau/\varrho_\infty)$, we can state that J decreases monotonously when $|v_1|$ and/or τ become larger, and reaches zero when $|v_1|\,\tau$ goes to infinity.

II.5) Conservation of Information

Till now we only asked for an averaged amount of information we get by doing a measurement. To be straight forward, the next question is: How long are chemical reaction systems able to conserve a special message just detected by measurement? For this purpose, quite analogously to the definition of the information gain in Chapter I, we determine information loss in the following way: The uncertainty of the event that the system is in microstate φ_i, is given by $-\,\text{ld}\, p_{i,\text{detect}}$ just after the measurement (finished at time t_*) and by $-\,\text{ld}\, p_i(t)$ for later times t (where $p_i(t)$ obeys the initial condition $p_i(t_*) = p_{i,\text{detect}}$). By averaging $(\text{ld}\, p_i(t) - \text{ld}\, p_{i,\text{detect}})$ with respect to $P_{N,\text{detect}}$, we get the negative of the increase of uncertainty, i.e., the loss of the information that was contained in the detected message $P_{N,\text{detect}}$:

$$S(P_N(t)/P_{N,\text{detect}}) = \sum_{i=1}^{N} p_{i,\text{detect}}\,\text{ld}\,\frac{p_i(t)}{p_{i,\text{detect}}}\,. \tag{31}$$

Adding $S(P_N(t)/P_{N,\text{detect}})$ and $K(P_{N,\text{detect}}/P_{N,\infty})$, averaging over all possible detector outputs $P_{N,\text{detect}}(j)$, and translating into the language of continuous variables, we then have the quantity

$$J(\alpha/\varrho_\infty; t - t_*) = \int_{-\infty}^{+\infty} \text{d}z\,\varrho_{\text{d}}(z) \int_0^1 \varrho_{\text{detect}}(x/z)\,\text{ld}\,\frac{\varrho(x;t)}{\varrho_\infty(x)}\,\text{d}x\,, \tag{32}$$

where $\varrho(x;t)$ is developed by the stochastics of the reaction kinetics under the initial condition $\varrho(x;t_*) = \varrho_{\text{detect}}(x/z)$. The time dependence of this information measure describes the conservation of a message (detected at time t_*) by the reaction system at later times t, averaged over all possible messages the system might be able to communicate to us at t_* via a particular detector characterized by α.

For the evaluation of the expression (32), again we set $\varrho_{\text{d}}(z) = \varrho_\infty(z)$, $\varrho_{\text{detect}}(x/z) = \tilde{\varrho}(x; t_0 + \tfrac{1}{2}\tau)$, and $\varrho(x;t) = \tilde{\varrho}(x; t - \tfrac{1}{2}\tau)$ — for $t = t_* = t_0 + \tau$, $\varrho(x;t)$ must be equal to $\varrho_{\text{detect}}(x/z)$! — where $\tilde{\varrho}(x;t)$ obeys the initial condition $\tilde{\varrho}(x;t_0) = \delta(x - z)$. For the reaction scheme (8), the first and the second moment of $\tilde{\varrho}(x;t)$ are already written down in Equations (29). After some algebra, the integration of Eq. (32) yields

$$\begin{aligned} J(\tau/\varrho_\infty; t - t_*) &= -\tfrac{1}{2}\,\text{ld}\{1 - \exp[-2|v_1|(t - t_* + \tfrac{1}{2}\tau)]\} \\ &\quad + \tfrac{1}{2}(\ln 2)^{-1}\exp(-|v_1|\,\tfrac{1}{2}\tau) \\ &\quad \cdot \frac{1 - \exp[-|v_1|(t - t_*)]}{\sinh[|v_1|(t - t_* + \tfrac{1}{2}\tau)]}\,. \end{aligned} \tag{33}$$

The graphic representation of this quantity is shown in Figure 1.

Explicitly, it should be noted that the information measure (32) is not identical to an averaged K-functional,

$$\bar{K}(\varrho(t)/\varrho_\infty) = \int_{-\infty}^{+\infty} \text{d}z\,\varrho_{\text{d}}(z) \int_0^1 \varrho(x;t)\,\text{ld}\,\frac{\varrho(x;t)}{\varrho_\infty(x)}\,\text{d}x\,, \tag{34}$$

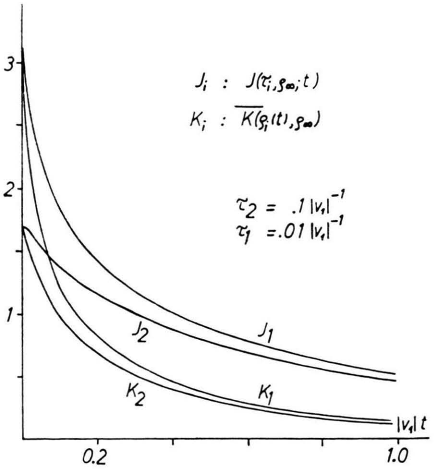

Fig. 1. The information measure $J(\tau/\varrho_\infty; t-t_*)$ representing conservation of a message within the open system considered, is shown as a function of the time interval being passed away since the message was detected. This information measure is influenced by the "sensibility" of the detector in such a way that, for any fixed time interval $t-t_*$, the amount of $J(\tau/\varrho_\infty; t-t_*)$ becomes greater if we use a detector with increased "sensibility" (i. e. $J(\tau/\varrho_\infty; t-t_*)$ is a monotonously decreasing function of τ!). For comparison, also the shape of the corresponding averaged K-functional is drawn.

where $\varrho(x; t)$ again fulfills $\varrho(x; t_*) = \varrho_{\text{detect}}(x/z)$. The main difference is that $J(\tau/\varrho_\infty; t-t_*)$ has a vanishing initial slope,

$$\frac{\mathrm{d}}{\mathrm{d}t} J(\tau/\varrho_\infty; t-t_*)\bigg|_{t=t_*} = 0\,, \tag{35}$$

whereas $\bar{K}$ starts already with a negative slope. Therefore, as is shown in Fig. 1 for the special reaction scheme (8), the information measure $J(\tau/\varrho_\infty; t-t_*)$ has values greater than those of $\bar{K}$ every where.

III. One-Component Reaction System with Bistability

The reaction kinetics of chemical reaction systems are generally much more complicated than was the case for the system treated just before. In order to attack some basic features of that more complex behaviour, it is, as already mentioned in the introduction of this paper, useful to consider reaction schemes exhibiting simple non-equilibrium phase transitions. We start with the scheme

$$A + 2X \underset{k^{(1)}_{\leftarrow}}{\overset{k^{(1)}_{\rightarrow}}{\rightleftharpoons}} 3X\,, \tag{36.1}$$

$$B + X \underset{k^{(2)}_{\leftarrow}}{\overset{k^{(2)}_{\rightarrow}}{\rightleftharpoons}} E \tag{36.2}$$

which was proposed [35] as a reaction model for a non-equilibrium phase transition of first order. Because of the trimolecular autocatalytic reaction step (36.1), here, we have to do with reaction kinetics of a non-linear kind. The rates for increase and decrease of the number of X-molecules are given by

$$R_{+X} = k^{(1)}_{\rightarrow}\, a\, x^2 + k^{(2)}_{\leftarrow}\, e\,, \tag{37a}$$

$$R_{-X} = k^{(1)}_{\leftarrow}\, x^3 + k^{(2)}_{\rightarrow}\, b\, x\,. \tag{37b}$$

Therefore, the rate equation $\mathrm{d}x/\mathrm{d}t = v(x)$ is of third order in x so that, in some regime of values of the concentrations a, b, c and of the reaction parameters k, it is possible to find three different stationary solutions of this rate equation, namely $x_{\mathrm{s},-}$, x_0, and $x_{\mathrm{s},+}$ with $x_{\mathrm{s},-} < x_0 < x_{\mathrm{s},+}$. But only the outer solutions $x_{\mathrm{s},-}$, $x_{\mathrm{s},+}$ correspond to stable steady states — the gradient of $v(x)$ is negative in the neighbourhoods of the points $x_{\mathrm{s},-}$, $x_{\mathrm{s},+}$ (see Fig. 2) so that small deviations from the stationary solutions will be removed by the reaction kinetics at once — whereas the solution x_0 is unstable against deviations.

As shown in Fig. 2, this bistability disappears and is replaced by only one stable stationary solution if the concentration of E is changed by a certain amount: With increasing e, $x_{\mathrm{s},-}$ and x_0 move together, by this $x_{\mathrm{s},-}$ becomes unstable and then disappears. For a decrease of e, the same is true for $x_{\mathrm{s},+}$ and x_0. If the steady state $x_{\mathrm{s},+}$ is

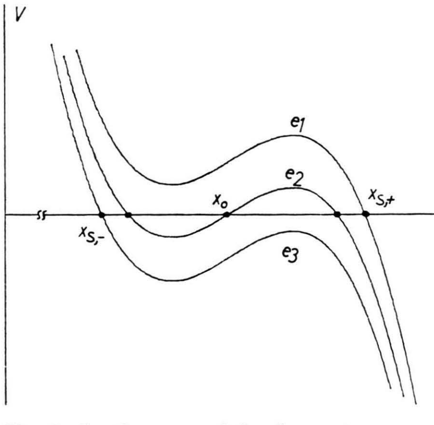

Fig. 2. In the case of fixed reaction parameters $k^{(\nu)}_{\rightleftharpoons}$ and fixed concentrations of the initial reaction partners A, B, the total reaction rate $v(x) = R_{+X} - R_{-X}$ of the intermediate molecules X is shown as a function of the X-concentration. For the concentration of the final substance E, we chose $e_1 > e_{\text{coex}}$, $e_2 = e_{\text{coex}}$, and $e_3 < e_{\text{coex}}$ (cf. Equation (38)).

denoted as phase I of the reaction system, and $x_{\mathrm{s},-}$ as phase II, then a similarity of the behaviour of these steady states to first order phase transitions [36] becomes apparent. Furthermore, when the space dependence of the x-variable and the effect of diffusion processes are really taken into account, one can prove [35] that the reaction model in question is able to show coexistence of phases I and II. The condition for coexistence can be formulated in a similar way as is done by the Maxwell construction in the case of the Van-der-Waals gas:

$$\left\{ \int_{x_{\mathrm{s},-}}^{x_0} v(x)\,\mathrm{d}x + \int_{x_0}^{x_{\mathrm{s},+}} v(x)\,\mathrm{d}x \right\} \Bigg|_{e=e_{\mathrm{coex}}} = 0 \tag{38}$$

(see also [4]).

III.1) Non-Equilibrium Phase Transition of Second Order; Order Parameter Concept

In the course of this paper, we are "interested" in another kind of phase transition that, e.g., occurs in the following way: Up to here only the concentration of E-molecules has been varied; we now fix e by the above coexistence condition and treat the dependence of the reaction system on the B-concentration for a given A-concentration. On the coexistence line, the steady states $x_{\mathrm{s},-}$ and $x_{\mathrm{s},+}$ are symmetrically placed around x_0,

$$x_{\mathrm{s},+} = x_0 + \Delta\,, \quad x_{\mathrm{s},-} = x_0 - \Delta \tag{39}$$

with

$$x_0 = \frac{1}{3}\,\frac{k^{(1)}_{\rightarrow}}{k^{(1)}_{\leftarrow}}\,a\,, \quad \Delta = \sqrt{\frac{1}{3}\left(\frac{k^{(1)}_{\rightarrow}}{k^{(1)}_{\leftarrow}}\,a\right)^2 - \frac{k^{(2)}_{\rightarrow}}{k^{(1)}_{\leftarrow}}\,b}$$

while e_{coex} is determined by

$$e_{\mathrm{coex}} = \frac{1}{3}\,\frac{k^{(1)}_{\rightarrow}}{k^{(2)}_{\leftarrow}}\,a \left\{ \frac{k^{(2)}_{\rightarrow}}{k^{(1)}_{\leftarrow}}\,b - \frac{2}{9}\left(\frac{k^{(1)}_{\rightarrow}}{k^{(1)}_{\leftarrow}}\,a\right)^2 \right\}. \tag{40}$$

Because of the concentrations being positive definite variables, b is bounded from below by $\frac{2}{9}\,\frac{(k^{(1)}_{\rightarrow}\,a)^2}{k^{(2)}_{\rightarrow}\,k^{(1)}_{\leftarrow}}$. With increase of b the square root Δ becomes smaller, goes through zero at $b_{\mathrm{c}} = \frac{1}{3}\,\frac{(k^{(1)}_{\rightarrow}\,a)^2}{k^{(2)}_{\rightarrow}\,k^{(1)}_{\leftarrow}}$, and then assumes purely imaginary values. Correspondingly, $x_{\mathrm{s},+}$ and $x_{\mathrm{s},-}$ move together, coincide with x_0 and then, because of their imaginary parts, lose their character as stationary solutions indicating steady states (see Fig. 3). Therefore, in the region $b > b_{\mathrm{c}}$, the only steady state remaining is given by x_0. (It should be noted that the Maxwell construction used above naturally is of no meaning in the region $b > b_{\mathrm{c}}$, but, as can be shown directly from $v(x)$, the results deduced by it (Eqs. (39) and (40)) can be continued into that region, giving just one branch of solutions being possible there.)

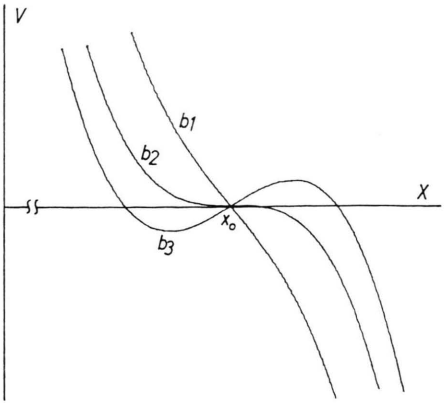

Fig. 3. The total reaction rate $v(x)$ versus the X-concentration in the case that the E-concentration is fixed by $e = e_{\mathrm{coex}}$ and the B-concentration is assumed to be a variable parameter: $b_1 > b_{\mathrm{c}}$, $b_2 = b_{\mathrm{c}}$, and $b_3 < b_{\mathrm{c}}$.

This abruptly changing behaviour of the steady state constellation at $b = b_{\mathrm{c}}$ makes it obvious to denote b_{c} as a "critical point" at which a second order phase transition [36, 4] takes place. The characteristic feature of this transition is some kind of symmetry breaking. This can be best visualized when writing the rate equation for the X-concentration in a form usual in time-dependent Landau theory [4],

$$\frac{\mathrm{d}}{\mathrm{d}t}\,q = -\frac{\mathrm{d}}{\mathrm{d}q}\,F(q)\,, \quad q =_{\mathrm{Def}} x - x_0\,, \tag{41}$$

where

$$F(q) = F_0 + \tfrac{1}{2}\,\alpha\,q^2 + \tfrac{1}{4}\,\beta\,q^4$$

F_0: arbitrary integration constant,

$$\alpha = -\,k^{(1)}_{\leftarrow}\,\Delta^2 = k^{(2)}_{\rightarrow}\,b - \frac{1}{3}\,\frac{(k^{(1)}_{\rightarrow}\,a)^2}{k^{(1)}_{\leftarrow}}\,,$$

$$\beta = +\,k^{(1)}_{\leftarrow}$$

is the non-equilibrium analogue of the free energy. In the language of the variable q, for $b > b_{\mathrm{c}}$, the steady state is given by $q_{\mathrm{s}} = 0$. At the critical point, this stationary solution becomes unstable and branches into two steady states ("bifurcation" of the stationary solution [3]) so that $q_{\mathrm{s},+} = \Delta$,

$q_{\mathrm{s},-} = -\Delta$ for $b < b_{\mathrm{c}}$. On the other hand, $F(q)$ is invariant against replacing q by $-q$ and, hence, also the differential equation (41) is. But just this inversion symmetry is broken by the solution of Eq. (41) within the regime $b < b_{\mathrm{c}}$, because $q(t)$ tends to either the steady state $x_{\mathrm{s},+}$ or the other one, $x_{\mathrm{s},-}$.

In order to have an indicator for the onset of symmetry breaking, in the Landau theory of equilibrium phase transitions [36], it is usual to introduce an order parameter which is zero above and has values different from zero below the critical point. In the non-equilibrium situation considered here, $q(t)$ is called the order parameter [4]. Treating its time-dependence in linear approximation, above the critical point, we obtain the relaxation behaviour

$$q_{\mathrm{lin}}(t) \sim e^{-\alpha t} . \tag{42}$$

When the system approaches the critical point this relaxation process becomes slower and slower ("critical slowing-down") and the steady state $q_{\mathrm{s}} = 0$ becomes unstable at the critical point $b = b_{\mathrm{c}}$ ($\triangleq \alpha = 0$). Since the non-equilibrium phase transition of the reaction system is connected to this instability we can say that the order parameter determines the character of the phase transition by the kind of its instability (cf. also Chapter V!).

III.2) Stochastic Treatment

We are not interested in a very accurate stochastic treatment of the reaction scheme in question [37] but rather in a calculation that incorporates the basic features. Starting with the Fokker-Planck equation (18), it is, as already mentioned in Sect. II.3, not sufficient to be contented with the system size expansion because we are willing to do the calculation within a range including also the non-equilibrium phase transition. Therefore, we have to deal with the hierarchy of equations for the moments given by Eqs. (25) and (26). By using $q = x - x_0$, so that

$$\begin{aligned} v(x) &= R_{+X} - R_{-X} \\ &= -k_{\leftarrow}^{(1)}(x - (x_0 - \Delta))(x - x_0)(x - (x_0 + \Delta)) \end{aligned}$$

can be written in the simpler form ($\alpha = -\Delta^2$)

$$v(q) = -\alpha q - q^3 \tag{43}$$

(for convenience, we choose the scale of the time coordinate so that $k_{\leftarrow}^{(1)}$ becomes equal to unity), we get for the lowest moments

$$\frac{\mathrm{d}}{\mathrm{d}t}\langle q\rangle = -\alpha\langle q\rangle - \langle q^3\rangle , \tag{44a}$$

$$\frac{\mathrm{d}}{\mathrm{d}t}\langle q^2\rangle = -2\alpha\langle q^2\rangle - 2\langle q^4\rangle + \frac{2}{V}D , \tag{44b}$$

$$\dots \tag{44c}$$

Here, we again approximate $D(x) = \frac{1}{2}(R_{+X} + R_{-X})$ by the constant value $D(x_0) =_{\mathrm{Def}} D$.

α) Moment Equations Above the Phase Transition Point

With only a single steady state existing in the regime $b > b_{\mathrm{c}}$, we approximate the probability distribution for the X-concentration within the reaction volume by a Gaussian form. Then the lowest moments of $\varrho(q;t)$ are

$$\begin{aligned} &\langle q\rangle =: \bar{q} , \quad \langle(q - \langle q\rangle)^2\rangle =: V^{-1}\sigma , \\ &\langle(q - \langle q\rangle)^3\rangle = 0 , \quad \text{and} \\ &\langle(q - \langle q\rangle)^4\rangle =: 3\,V^{-2}\sigma^2 . \end{aligned}$$

Inserting this by help of Eq. (26) into Eqs. (44), we get a closed system of differential equations for the time dependence of the first and the second moment of $\varrho(q;t)$:

$$\frac{\mathrm{d}}{\mathrm{d}t}\bar{q} = -\left(\alpha + \frac{3}{V}\sigma\right)\bar{q} - \bar{q}^3 , \tag{45a}$$

$$\frac{\mathrm{d}}{\mathrm{d}t}\sigma = -2(\alpha + 3\bar{q}^2)\sigma - \frac{6}{V}\sigma^2 + 2D . \tag{45b}$$

Comparing this result with the prior Eqs. (19) and (22), we find that the main difference is due to the time development of the variance σ because of its non-linearity. Together with $\lim_{t\to\infty}\bar{q}(t) = 0$, $\sigma(t)$ approaches the limiting value

$$\lim_{t\to\infty}\sigma(t) = \frac{1}{6}V\left\{\sqrt{\alpha^2 + 12\frac{D}{V}} - \alpha\right\}, \tag{46}$$

which reaches its maximum, $\sqrt{\frac{1}{3}VD}$, at the critical point b_{c} ($\triangleq \alpha = 0$) and is thus (for finite V!) bounded everywhere (see also [50]).

β) Stochastics in the Regime of Bistability

Because of the existence of two steady states for $b < b_{\mathrm{c}}$, here, we are confronted with the problem of metastable states [38, 49, 55] when going into the stochastics. This problem, however, can be roughly attacked by assuming the probability distribution $\varrho(q;t)$ to be a sum of two Gaussian distributions which are displaced from each other [39]:

$$\varrho(q;t) = c_\mathrm{l}(t)\,\varrho_\mathrm{l}(q;t) + c_\mathrm{r}(t)\,\varrho_\mathrm{r}(q;t) \tag{47}$$

with

$$c_\mathrm{r}(t) = 1 - c_\mathrm{l}(t); \quad \int\limits_{-\infty}^{+\infty} \varrho_j(q;t)\,\mathrm{d}q = 1, \quad j = \mathrm{l}, \mathrm{r};$$

where $\varrho_\mathrm{l}(q;t)$ is assigned to the left-hand side and $\varrho_\mathrm{r}(q;t)$ to the right-hand side steady state. The weight factors $c_\mathrm{l}(t)$, $c_\mathrm{r}(t)$ may be defined by

$$c_\mathrm{l}(t) = \int\limits_{-\infty}^{0} \varrho(q;t)\,\mathrm{d}q \tag{48}$$

and $c_\mathrm{r}(t)$ correspondingly. Then, by integration of the Fokker-Planck equation (18), we get the time dependence of $c_\mathrm{l}(t)$ by

$$\begin{aligned}\frac{\mathrm{d}}{\mathrm{d}t} c_\mathrm{l}(t) &= - v(q)\,\varrho(q;t)\Big|_{-\infty}^{0} + \frac{D}{V}\frac{\partial}{\partial q}\varrho(q;t)\Big|_{-\infty}^{0} \\ &= D\left\{c_\mathrm{l}(t)\frac{\bar{q}_\mathrm{l}(t)}{\sigma_\mathrm{l}(t)}\varrho_\mathrm{l}(0;t) + c_\mathrm{r}(t)\frac{\bar{q}_\mathrm{r}(t)}{\sigma_\mathrm{r}(t)}\varrho_\mathrm{r}(0;t)\right\},\end{aligned} \tag{49}$$

where $\bar{q}_j$, σ_j are the first and the second moment of $\varrho_j(q;t)$, $j = \mathrm{l}, \mathrm{r}$.

For this doubly peaked distribution $\varrho(q;t)$, the first-moment equation (44a) becomes

$$\begin{aligned}\sum_{j=\mathrm{l},\mathrm{r}} c_j \frac{\mathrm{d}}{\mathrm{d}t}\bar{q}_j &= \sum_{j=\mathrm{l},\mathrm{r}} c_j\left[-\left(\alpha + \frac{3}{V}\sigma_j\right)\bar{q}_j - \bar{q}_j{}^3\right] \\ &\quad - \left(\frac{\mathrm{d}}{\mathrm{d}t}c_\mathrm{l}\right)(\bar{q}_\mathrm{l} - \bar{q}_\mathrm{r}).\end{aligned} \tag{50}$$

In order to decouple $\bar{q}_\mathrm{l}$ and $\bar{q}_\mathrm{r}$, we make the Ansatz

$$\frac{\mathrm{d}}{\mathrm{d}t}\bar{q}_j = [j] + \dot{Q}_j, \quad j = \mathrm{l}, \mathrm{r},$$

where the $\dot{Q}_j$ represent those parts of the variation of $\bar{q}_j$ which are exclusively due to the exchange of "probability mass" between $\varrho_\mathrm{l}(q;t)$ and $\varrho_\mathrm{r}(q;t)$. From the balance equations

$$\begin{aligned}&\lim_{\tau\to 0} c_\mathrm{r}(t+\tau)\,\{\bar{q}_\mathrm{r}(t) + \tau\dot{Q}_\mathrm{r}\} \\ &\quad\cdot = c_\mathrm{r}(t)\,\bar{q}_\mathrm{r}(t) - \lim_{\tau\to 0}\tau\, q_t \frac{\mathrm{d}}{\mathrm{d}t}c_\mathrm{l},\end{aligned} \tag{51a}$$

$$\begin{aligned}&\lim_{\tau\to 0} c_\mathrm{l}(t+\tau)\,\{\bar{q}_\mathrm{l}(t) + \tau\dot{Q}_\mathrm{l}\} \\ &\quad\cdot = c_\mathrm{l}(t)\,\bar{q}_\mathrm{l}(t) + \lim_{\tau\to 0}\tau\, q_t \frac{\mathrm{d}}{\mathrm{d}t}c_\mathrm{l},\end{aligned} \tag{51b}$$

where $\lim\limits_{\tau\to 0}\tau\frac{\mathrm{d}}{\mathrm{d}t}c_\mathrm{l}$ is the amount of "probability mass" that is given from $\varrho_\mathrm{r}(q;t)$ to $\varrho_\mathrm{l}(q;t)$ at point $q = q_t$ and time t, and by putting q_t into the middle between both steady states, $q_t = 0$, we get

$$\dot{Q}_\mathrm{r} = \left(\frac{\mathrm{d}}{\mathrm{d}t}c_\mathrm{l}\right)\frac{\bar{q}_\mathrm{r}(t)}{c_\mathrm{r}(t)}, \quad \dot{Q}_\mathrm{l} = -\left(\frac{\mathrm{d}}{\mathrm{d}t}c_\mathrm{l}\right)\frac{\bar{q}_\mathrm{l}(t)}{c_\mathrm{l}(t)}. \tag{52}$$

After transformation to the variables $\xi_\mathrm{r} = q - \varDelta$ and $\xi_\mathrm{l} = q + \varDelta$ measuring the deviations from the steady states $q_{\mathrm{s},+}$ and $q_{\mathrm{s},-}$, respectively, the first-moment equations appear as

$$\begin{aligned}\frac{\mathrm{d}}{\mathrm{d}t}\bar{\xi}_\mathrm{r} &= \left(\frac{\dot{c}_\mathrm{l}}{c_\mathrm{r}} - \frac{3}{V}\sigma_\mathrm{r}\right)\varDelta \\ &\quad - \left(2\varDelta^2 + \frac{3}{V}\sigma_\mathrm{r} - \frac{\dot{c}_\mathrm{l}}{c_\mathrm{r}}\right)\bar{\xi}_\mathrm{r} - 3\varDelta\,\bar{\xi}_\mathrm{r}{}^2 - \bar{\xi}_\mathrm{r}{}^3,\end{aligned} \tag{53a}$$

$$\begin{aligned}\frac{\mathrm{d}}{\mathrm{d}t}\xi_\mathrm{l} &= \left(\frac{\dot{c}_\mathrm{l}}{c_\mathrm{l}} + \frac{3}{V}\sigma_\mathrm{l}\right)\varDelta \\ &\quad - \left(2\varDelta^2 + \frac{3}{V}\sigma_\mathrm{l} + \frac{\dot{c}_\mathrm{l}}{c_\mathrm{l}}\right)\bar{\xi}_\mathrm{l} + 3\varDelta\bar{\xi}_\mathrm{l}{}^2 - \bar{\xi}_\mathrm{l}{}^3\end{aligned} \tag{53b}$$

with $\dot{c}_\mathrm{l} = \frac{\mathrm{d}}{\mathrm{d}t}c_\mathrm{l}$.

In the case of the second-moment equations to be derived from Eq. (44b), we succeed with the corresponding Ansatz

$$\frac{\mathrm{d}}{\mathrm{d}t}\sigma_j = \left[-2(\alpha + 3\,\bar{q}_j{}^2)\,\sigma_j - \frac{6}{V}\sigma_j{}^2 + 2D\right] + \dot{\Sigma}_j, \quad j = \mathrm{l}, \mathrm{r},$$

(cf. Eq. (45b) and note that both the $\varrho_j(q;t)$ are assumed to be of Gaussian form again). Setting up balance equations now for $\langle q^2\rangle$ in the same manner as done for $\langle q\rangle = c_\mathrm{r}(t)\,\bar{q}_\mathrm{r}(t) + c_\mathrm{l}(t)\,\bar{q}_\mathrm{l}(t)$ by Eqs. (51), we get for the rate of change of the variances σ_j due to the exchange of "probability mass"

$$\begin{aligned}\dot{\Sigma}_\mathrm{r} &= \frac{\dot{c}_\mathrm{l}}{c_\mathrm{r}}(\sigma_\mathrm{r} - V\bar{q}_\mathrm{r}{}^2); \\ \dot{\Sigma}_\mathrm{l} &= -\frac{\dot{c}_\mathrm{l}}{c_\mathrm{l}}(\sigma_\mathrm{l} - V\bar{q}_\mathrm{l}{}^2).\end{aligned} \tag{54}$$

Transforming again to ξ_r, ξ_l, we arrive at the second-moment equations

$$\begin{aligned}\frac{\mathrm{d}}{\mathrm{d}t}\sigma_\mathrm{r} &= \left\{2D - V\frac{\dot{c}_\mathrm{l}}{c_\mathrm{r}}(\bar{\xi}_\mathrm{r} + \varDelta)^2\right\} \\ &\quad - 2\left\{3(\bar{\xi}_\mathrm{r} + \varDelta)^2 - \varDelta^2 - \frac{\dot{c}_\mathrm{l}}{2c_\mathrm{r}}\right\}\sigma_\mathrm{r} - \frac{6}{V}\sigma_\mathrm{r}{}^2,\end{aligned} \tag{55a}$$

$$\begin{aligned}\frac{\mathrm{d}}{\mathrm{d}t}\,\sigma_{\mathrm{l}} &= \left\{2D + V\,\frac{\dot{c}_{\mathrm{l}}}{c_{\mathrm{l}}}\,(\bar{\xi}_{\mathrm{l}} - \varDelta)^2\right\} \\ &\quad - 2\left\{3\,(\bar{\xi}_{\mathrm{l}} - \varDelta)^2 - \varDelta^2 + \frac{\dot{c}_{\mathrm{l}}}{2c_{\mathrm{l}}}\right\}\sigma_{\mathrm{l}} - \frac{6}{V}\,\sigma_{\mathrm{l}}^2\,. \end{aligned} \tag{55b}$$

The limiting values of the first and second moments can be found by help of the following argument: The stationary solution of the Fokker-Planck equation (18) has the form $\varrho_\infty(q) \sim \exp(-F(q)\cdot V/D)$ [4] — remember our approximation $D(x) = D$ — where $F(q)$ is the generalized thermodynamic potential already introduced in Equation (41). Thus, the limiting distribution has the same inversion symmetry as $F(q)$ has, i.e., the variances of the single Gaussians $\varrho_{\mathrm{r},\infty}(q)$, $\varrho_{\mathrm{l},\infty}(q)$ are equal to each other, $\sigma_{\mathrm{r},\infty} = \sigma_{\mathrm{l},\infty}$, and also the weight factors are $c_{\mathrm{r},\infty} = c_{\mathrm{l},\infty} = \frac{1}{2}$, whereas the mean values obey the condition $\bar{\xi}_{\mathrm{r},\infty} = -\bar{\xi}_{\mathrm{l},\infty}$. Obviously, in this case, the "probability mass" flow between ϱ_{r} and ϱ_{l} is balanced, i.e., $\lim\limits_{t\to\infty} \dot{c}_{\mathrm{l}} = 0$, as can be seen also directly from Equation (49). From Eqs. (53) and (55), then we get

$$\begin{aligned}\lim_{t\to\infty} \bar{\xi}_{\mathrm{l}} &= -\lim_{t\to\infty} \bar{\xi}_{\mathrm{r}} \\ &= \varDelta - \sqrt{\tfrac{1}{2}\left(\varDelta^2 + \sqrt{\varDelta^4 - 6D/V}\right)}\,, \end{aligned} \tag{56}$$

$$\lim_{t\to\infty} \sigma_{\mathrm{r,l}} = \tfrac{1}{6}\,V\left\{\varDelta^2 - \sqrt{\varDelta^4 - 6D/V}\right\}. \tag{57}$$

This result demonstrates, firstly, that the limiting values of the first moments, $\bar{q}_{\mathrm{r},\infty}$ and $\bar{q}_{\mathrm{l},\infty}$, do not exactly coincide with the steady states calculated by deterministic reaction kinetics and, secondly, that the "double Gaussian" approximation for $\varrho(q;t)$ breaks down in the very critical regime because the expressions for $\bar{\xi}_{j,\infty}$, $\sigma_{j,\infty}$, $j = \mathrm{l}, \mathrm{r}$, become complex numbers within the region $0 < \varDelta < \sqrt[4]{6D/V}$. If one wants to get also a description of the nearest neighbourhood of the non-equilibrium phase transition one has to think about better approximations, but this is not necessary in the course of this paper.

γ) Time Scales of the Relaxation Process

As a last point, we shortly discuss the different time scale behaviour of the relaxation of $\varrho(q;t)$ to $\varrho_\infty(q)$. As can be seen immediately from Eqs. (53) and (55), the single peak parts $\varrho_{\mathrm{r}}(q;t)$ and $\varrho_{\mathrm{l}}(q;t)$ approach $\varrho_{\mathrm{r},\infty}(q)$ and $\varrho_{\mathrm{l},\infty}(q)$, respectively, on the same time scale as $\varrho(q;t)$ runs into the single peaked distribution $\varrho_\infty(q)$ above the critical point (cf. Eqs. (45)), namely on a scale proportional to $|\alpha|^{-1} = |\varDelta^2|^{-1}$ if the system is outside of its very critical regime, $|\alpha|$, $|\varDelta^2| \gg \sqrt{D/V}$, and proportional to $\sqrt{V/D}$ near the critical point. (Remember the critical slowing down mentioned in Sect. III.1 which is responsible for that increase of the time scale near the critical point.) The situation is quite different when we start with a single peaked distribution $\varrho(q;t) = \varrho_{\mathrm{r},\infty}(q)$ (or $\varrho_{\mathrm{l},\infty}(q)$) and ask for the time necessary for $\varrho(q;t)$ to approach the double peaked limiting distribution $\varrho_\infty(q)$, i.e., we ask for the life time of these "almost steady" states (which are metastable because of the stochastics). According to Eq. (49), the mass flow transporting "probability mass" from the initially existing distribution peak to the other peak to be built up, in leading order, is proportional to $\exp[-(\varDelta^4/D)\,V]$. Therefore the life time of the metastable states scales with $\exp[(\varDelta^4/D)\,V]$ [37].

III.3. Non-Equilibrium Phase Transition in the Picture of Information Theory

By numerically doing the integration of the differential equations (45) for $b > b_{\mathrm{c}}$, respectively, (49), (53), (55) for $b < b_{\mathrm{c}}$, and the calculation of the expressions (7), (32) in the same manner as in Sect. II.4 and II.5, we get the information measures $J(\tau/\varrho_\infty)$ and $J(\tau/\varrho_\infty; t - t_*)$ shown in Figs. 4 and 5. These graphs demonstrate the basic features of the second order non-equilibrium phase transition in a unified picture:

1. Within the critical regime, there is a dramatic increase of the averaged information we can detect by measurement, $J(\tau/\varrho_\infty)$, i.e., the reaction system here is characterized by "great variability". The reason is that the fluctuations of the X-concentration become large near the critical point.

2. On the other hand, the information conservation measure $J(\tau/\varrho_\infty; t - t_*)$ which is reduced by the initial value $J(\tau/\varrho_\infty)$ in Fig. 5, decreases more slowly in time t near the critical point than in the region above the phase transition. This has to do with the phenomenon of critical slowing down, i.e., the dynamics of the fluctuations slacken more and more.

3. Below the phase transition, $J(\tau/\varrho_\infty)$ again falls down, but is bounded from below by the level of one "bit" corresponding to the alternative that the system fluctuates — now again in a normal

manner as was the case above the critical region — around either the right-hand side or the left-hand side steady state.

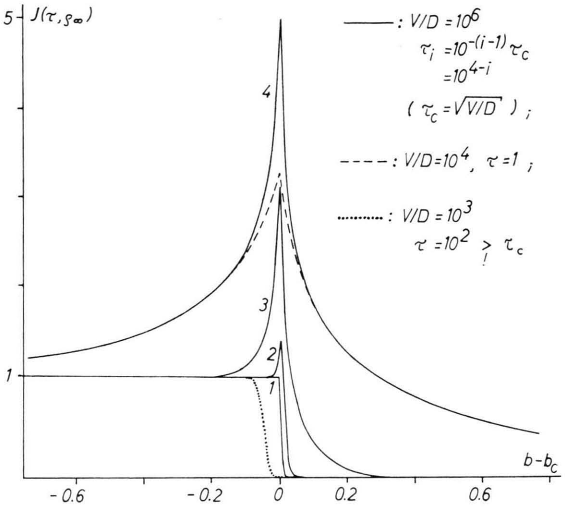

Fig. 4. For the one-component reaction system (36), the information measure $J(\tau/\varrho_\infty)$ is shown as a function of the difference between the actual B-concentration and the B-concentration at the critical point, for various values of V/D and for different "sensibilities" (i.e. different values of τ) of the detector. In order to avoid that the shape of $J(\tau/\varrho_\infty)$ depends on other variables than $b-b_c$, V, D, and τ, we reduced the scales of the time-coordinate and the B-concentration so that $k_-^{(1)}$ and, respectively, $k_-^{(2)}$ become equal to unity (cf. Equation (41)).

Apart from the remarks made within the text, the following facts additionally should be mentioned at this place:

1) The numerical calculations support the conjecture that the information measure considered depends on V and D in leading order only via the ratio V/D,

2) For fixed τ, the maximum of $J(\tau/\varrho_\infty)$ localized at $b \simeq b_c$ grows with increasing ratio V/D and logarithmically diverges if V/D goes to infinity (see the dashed curve and curve 4).

3) With decreasing "detector sensibility", $J(\tau/\varrho_\infty)$ falls down along the whole b-axis and approaches a step-function (see curve 1) when τ reaches the value of the critical relaxation time τ_c. Thus, for $\tau \simeq \tau_c$, the detector does not "see" the concentration fluctuations any longer and records only the onset of the bifurcation into two metastable steady states, indicating this by the jump of $J(\tau/\varrho_\infty)$ from zero to the one-bit level at $b \simeq b_c$.

4) If the characteristic time of the detector, τ, is larger than τ_c, then $J(\tau/\varrho_\infty)$ reaches its one-bit level not before b is some distance below b_c (see the dotted curve). For $\tau \gg \tau_c$, from the kinetic behaviour of Eq. (49), we can estimate this shift by $b_{1\text{-bit}} - b_c = -\sqrt{(D/V)(1 + \ln \tau/\tau_c)}$. (Since the "double Gaussian" approximation breaks down in the region $-\sqrt{6D/V} \leqq b - b_c \leqq 0$, the dotted curve which is numerically generated by an interpolation procedure bounded by the $(b > b_c)$- and the $(b < b_c - \sqrt{6D/V})$-properties of $J(\tau/\varrho_\infty)$, surely is quantitatively not quite correct, but it is expected to approximate the real shape of $J(\tau/\varrho_\infty)$ in a qualitatively sufficient manner.)

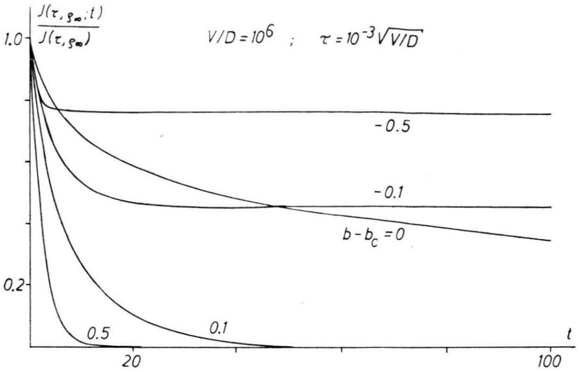

Fig. 5. The information conservation measure $J(\tau/\varrho_\infty; t - t_*)$ is drawn as a function of the time interval being passed away since the detector measurement was done. To guarantee again that the shape of $J(\tau/\varrho_\infty; t - t_*)$ depends only on the variables $b - b_c$, V, D, τ, and $t - t_*$, we rescaled the time- and the b-coordinate in the same manner as we did for Fig. 4. Since $J(\tau/\varrho_\infty; 0)$ $(= J(\tau/\varrho_\infty))$ strongly depends on the value of $b - b_c$ (cf. curve 4 of Fig. 4), we reduced also the $J(\tau/\varrho_\infty; t - t_*)$-scale by $J(\tau/\varrho_\infty)$ in order to demonstrate that the rate of the "information distruction" also is a strong function of $b - b_c$.

4. Quite analogously, $J(\tau/\varrho_\infty; t - t_*)$ also decreases more quickly, but lingers at the one-"bit" level and goes to zero only on a larger time scale due to the life time of the metastable steady states.

IV. Degree of Order and Its Meaning for Self-Organization of Matter

Till now we were interested in a theory for measurement of the quantity of "information": When dealing with stochastic reaction kinetics in some detail up to here, this was only necessary in order to exhibit actual values of the information measures, and their dependences from outer parameters, which we would have obtained when actually doing the corresponding experiments!

Let us now imagine the situation that we are confronted with the curves of the information measures for a special reaction system and that we are asked to characterize the system without using arguments based on stochastic reaction kinetics. This situation is in some way similar to problems in quantum theory and, thus, we shall proceed in a manner which is usual there: we search out "good quantum numbers", i.e., we look for quantities that are conserved. If we neglect the long-time-scale ($\sim \exp(c\,V)$!) behaviour, for the reaction system (36), we can state: As a function of the

B-concentration (and the E-concentration fixed by Eq. (40)), the system has two phases, the upper one showing no conservation of information, whereas the lower one is able to store just one "bit". Since the quantity "information" contains the structure being present within the system in an integral form (as mentioned in the introduction), in the lower phase regime, there must exist an observable that has two "eigenstates", and the system must be in one of these states. (This is quite analogous to a simple "yes"-or-"no"-alternative stored by the memory of a computer.)

That, however, is all the "information measure" can tell us. If we additionally want to learn what the physical meaning of the observable is and what state is taken on by the system, we have to do further experiments: In the case of the reaction system (36), we already know that the "eigenstates" represent normal fluctuations of the X-concentration around one of the metastable steady states at a time, which have become quasi stable by cutting off the long-time-scale behaviour, and that the quasi-conserved observable can be identified, e.g., with the difference between the actual (metastable) mean value of the X-concentration and the first moment of the truly stationary solution uniquely defined by the boundary conditions:

$$Q = \int q\, \varrho_{j,\infty}(q)\, \mathrm{d}q - \int q\, \varrho_{\infty}(q)\, \mathrm{d}q\,,$$

with j equal to either l or r.

IV.1. Self-Organization of the Reaction System Itself

A chemical reaction system, microscopically, constitutes a many-body problem, and this is manifested by the concentration fluctuations spontaneously arising. On the other hand, in the lower phase regime, there additionally is some kind of cooperativity — as is indicated by the feed-back loops which appear when we translate the autocatalytic reaction step into the language of electrical networks [40] — which instructs the whole ensemble of particles within the reaction volume to perform concentration fluctuations only around one of the steady states. However, from the outside, there is no possibility to prescribe to the system to which steady state it shall go, except if we suspend the requirement of the X-concentration moving freely, for a moment.

This (bifurcation) is just one basic feature of self-organization: By going beyond the phase transition, the system becomes cooperative and exhibits corresponding macroscopic and (quasi) stationary inner degrees of freedom. According to an initial fluctuation, the system itself ,,decides'' what state it will approach. Remembering the order parameter concept, we can further state: The onset of cooperativity is indicated by the instability of the order parameter. Because of the symmetry beaking followed by this instability, the phase below the phase transition is called the ordered phase — contrary to the disordered phase above the transition. (For this terminology see also [1, 3, 4, 36]!) To measure mathematically the degree of the order, i.e., the complexity of the phase structure caused by the symmetry breaking, the multiplicity of the "eigenstates" being possible within the phase, i.e., the exponent of the number of possible "eigenstates", $n = 2^{\nu}$, can be taken, and by this the quantity "degree of order" becomes numerically equivalent to the amount of information being conserved.

IV.2. Organization Induced by the Reaction System; Network Theory

Summarizing the preceding discussion, we can say that, with continuously decreasing B-concentration (a being fixed and e varying according to Eq. (40)!), the reaction scheme (36) works as a "generator of randomness" with just one alternative. Therefore, this system is suited to do its job as a "switching engine" within a chemical network. For this purpose, the following points are important:

i) Since the reaction kinetics of the reaction system (36) shall be unchanged, the other elements of the network must be coupled to that system in a way that the X-molecules take part in the subsequent reaction steps only as catalysers.

ii) As in the case for electrical circuits, also here, adaptation problems are present. They are connected to the slowness of the coupled network elements: If these elements react upon variations of the X-concentration very quickly, the whole network would start to rumble when the fluctuations of the X-concentration become large, i.e., when the "switching engine" goes beyond its phase transition. Or in the language of "information": Because of the constant coupling between "engine" and the other network elements, according to the dramatic increase of the amount of momentary information the reaction system (36) shows within its critical region (as indicated, e.g., by doing the temporally limited measurements by the detector, see Sect. III.3!), the "engine" permanently flings new messages into the network, each message being valid for a time interval at most of order $\sqrt{V/D}$ (as follows from the information conservation curves, see also Sect. III.2.γ!). However, if the response of the network elements becomes slower and slower, then even in the critical regime, this turbulence within the network diminishes and finally totally disappears, for the same reason that the information measure $J(\tau/\varrho_\infty)$ decreases for increasing measurement duration, τ, of the detector.

iii) Requiring the network elements to be as slow as to maintain smoothness also in the critical regime of the "engine", we may ask for the amount of variation of the B-concentration necessary for the "switching engine" to be able to organize the network according to its own self-organization, in such a way that each of its "eigenstates" instructs the network to be in a definite constellation determined solely by the "eigenstate" in question. From the considerations concerning the information measure $J(\tau/\varrho_\infty)$ of Fig. 4, for this b-variation, we can estimate a lower bound of the order of $\sqrt{D/V}$. If the characteristic time scale of the coupled network elements, τ, however, is much greater than the critical relaxation time of the "engine", $\tau_c \sim \sqrt{V/D}$, then this lower bound is also increased, and that by the same law as that of the expression $b_{1-\mathrm{bit}} - b_c$ given in the text below Figure 4.

To be more concrete, we consider a simple network showing already the properties just outlined (see Figure 6):

$$\mathrm{I} \underset{\mathrm{X}}{\rightarrow} \mathrm{H}, \quad \mathrm{H} \rightarrow \mathrm{I} \quad \text{(buffer)}, \tag{58}$$

$$\mathrm{C} + \mathrm{D} \underset{\mathrm{H}}{\rightarrow} \mathrm{F} \quad \text{(production)}. \tag{59}$$

Here, the reaction scheme (36) regulates the production rate of F-molecules via catalysing the substance H which is in turn necessary as a catalyser for the synthesis of C and D into F. In order to stabilize the H-concentration against the X-fluctuations, and hence the rate of the F-production, the rate parameters of the reaction steps (58) must be very small so that the relaxation of the H-concentration, h, given by

$$\frac{\mathrm{d}}{\mathrm{d}t} h = k_{\mathrm{I}\to\mathrm{H}} \cdot x \cdot i - k_{\mathrm{H}\to\mathrm{I}} \cdot h \,, \tag{60}$$

is slower than the critical regime relaxation of the X-fluctuations, i.e., $k_{\mathrm{I}\to\mathrm{H}}$, $k_{\mathrm{H}\to\mathrm{I}}$ must be of order $\sqrt{D/V}$.

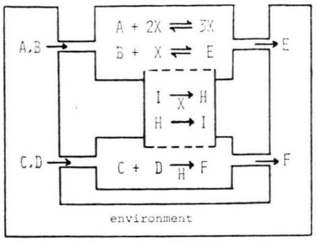

Fig. 6. A simple chemical network is sketched that contains the one-component reaction system (36) as an "information generator". Explicitely, it should be mentioned that the reaction steps noted in the above diagram generally are not to be read as real chemical reaction steps, but rather as shortened forms which just reflect the dominant processes within the reaction kinetics of a real reaction system. Especially the reaction steps that couple the "information pump" to the "synthesis process" $\mathrm{C} + \mathrm{D} \rightarrow \mathrm{F}$, can possibly represent a chemical system which constitutes again an open system far away from thermal equilibrium itself.

Let us try to describe the behaviour of the coupled system (36)–(58)–(59) in words of daily life situations: For $b > b_c$, the environment is intact and there is no question for the boss ("switching engine") about the production rate. Gradually, the environment goes bad. The boss becomes restless, but still his worries are buffered by the personnel so that the production is not affected. Finally, the situation becomes precarious; the boss has to take his decision, and he does. With some retardation, the personnel adjusts the production rate according to the boss's order.

To tell the truth, there is another difficulty that has to be noted. Till now we treated the process of buffering only by its deterministic reaction kinetics. As already demonstrated in Sect. II, the spontaneous fluctuations of the H-concentration produced within the buffer itself become more and more important with decreasing reaction parameters (see Sect. II.4). We can overcome this problem and make these fluctuations negligibly small compared to the concentration average if we enlarge the partial volume belonging to the buffer so that this volume becomes much greater than the partial volume of the "switching engine". It is, however, beyond the scope of this paper to go into further details of network theory. Therefore, we end the discussion of bistable reaction systems at this point.

V. Oscillating Reaction System with Limit Cycle

A reaction scheme par exellence showing limit cycle behaviour is given by [41]

$$A \rightleftharpoons X \qquad B + X \rightleftharpoons Y + E$$
$$2X + Y \rightleftharpoons 3X \qquad X \rightleftharpoons F \tag{61}$$

called the trimolecular model or the Brusselator [42]. (For a detailed description of the model see [3, 4, 5].) But there is a number of other possible reaction systems with two intermediates also exhibiting limit cycles [43]. In this section, we are not interested in the oscillating behaviour of one concrete model system, but rather in the basic components necessary for a limit cycle (for a systematic treatment see also [51]).

V.1) Superposition of Oscillation and Bistability

To start with, we consider the so-called Lotka-Volterra model [44, 45]

$$\begin{aligned} A_{\mathrm{LV}} + X &\rightarrow 2X\,, \\ X + Y &\rightarrow 2Y\,, \\ B_{\mathrm{LV}} + Y &\rightarrow E_{\mathrm{LV}} \end{aligned} \tag{62a}$$

which, in ecology, is well known as a model representing the population dynamics in a predator-prey system [46]. Setting the reaction parameters of the three irreversible reaction steps equal to k_{LV}, the rate equations

$$\begin{aligned} \mathrm{d}x/\mathrm{d}t &= k_{\mathrm{LV}}(a\,x - x\,y), \\ \mathrm{d}y/\mathrm{d}t &= k_{\mathrm{LV}}(x\,y - b\,y) \end{aligned} \tag{63}$$

admit, except for the trivial solution $x_0 = y_0 = 0$, the stationary solution

$$x_0 = b, \quad y_0 = a\,. \tag{64}$$

Within the vocabulary of stability analysis, this solution is not a (stable or unstable) focus, but a center: If the initial values of x and y do not coincide with x_0 and y_0, respectively, $x(t)$ and $y(t)$ move around that stationary solution in a closed loop, never reaching the center [2, 3, 5]. This behaviour is called a conservative concentration oscillation. Linearizing Eqs. (63) for small deviations from x_0, y_0, $q_x = x - x_0$ and $q_y = y - y_0$:

$$\mathrm{d}q_x/\mathrm{d}t = -\,k_{\mathrm{LV}}\,x_0\,q_y\,, \quad \mathrm{d}q_y/\mathrm{d}t = k_{\mathrm{LV}}\,y_0\,q_x\,, \tag{63a}$$

in the case of $x_0 = y_0$, these loops degenerate to simple circles.

Due to the reaction scheme (62a), none of the concentric loops being possible is distinguished. In order to get a limit cycle, however, this kind of invariance of the reaction system has to be removed, as, e.g., would be the case if some appropriate other reaction steps also become active within the reaction volume, entering into competition with the reaction (62a). Here, we assume this competitor to be the reaction system already discussed in Section III:

$$A_{C,X} + 2X \rightleftharpoons 3X, \quad B_{C,X} + X \rightleftharpoons E_{C,X}\,. \tag{62b}$$

Its influence on the kinetics of the total reaction is quite obvious: the originally closed loops become perturbed, spiral out, and approach a limiting loop (i.e., the limit cycle) that is favoured due to the steady state constellation of the reaction (62b), as to be shown in detail for a special case in the following.

To get a more symmetrical problem, we additionally assume a second competitor analogous to that of (62b), but acting on the intermediate substance Y,

$$A_{C,Y} + 2Y \rightleftharpoons 3Y, \quad B_{C,Y} + Y \rightleftharpoons E_{C,Y}\,. \tag{62c}$$

Furthermore, we adjust the concentrations of the initial and the final substances so that the reactions (62b) and (62c) work on their coexistence-lines [cf. Eqs. (39), (40)] and that their unstable (middle) stationary solutions, $x_{0,\mathrm{c}}$ and $y_{0,\mathrm{c}}$, respectively, become identical with the coordinates of the center of the Lotka-Volterra reaction, x_0 and y_0, which, in turn, we also require to be equal, $x_0 = y_0$. Under these special circumstances, the rate equations of the total reaction system look like (cf. Eqs. (43), (63a))

$$\frac{\mathrm{d}}{\mathrm{d}t}\,q_x = -\,\omega\,q_y + k_{\mathrm{c}}(\Delta^2 - q_x^2)\,q_x\,, \tag{65a}$$

$$\frac{\mathrm{d}}{\mathrm{d}t}\,q_y = \omega\,q_x + k_{\mathrm{c}}(\Delta^2 - q_y^2)\,q_y\,, \tag{65b}$$

where k_{c} is the parameter for the backward reaction of the first reaction step in (62b), as well as that in (62c), and $\omega = k_{\mathrm{LV}}\,x_0$.

The result of the numerical integration of the differential equations (65) is drawn in Fig. 7 where we used the reduced variables $\tilde{q}_x = q_x/\Delta$ and $\tilde{q}_y = q_y/\Delta$. Reducing also the time variable t by $\tilde{t} = \omega t$, the differential equations (65) then only contain the parameter $\gamma = k_{\mathrm{c}}\Delta^2/\omega$. Thus the form of the limit cycle obtained is exclusively determined by this parameter: For small γ, the limit cycle

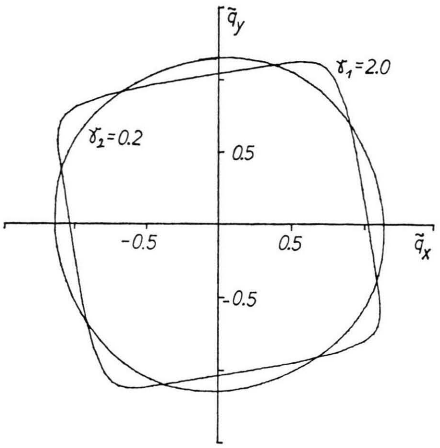

Fig. 7. For two values of $\gamma = k_c \Delta^2 \omega^{-1}$, the limit cycles resulting from the differential equations (65) are plotted.

almost is a circle (in this regime, the reaction system is dominated by the Lotka-Volterra reaction steps!) whereas it deviates from the circle more and more with increasing γ. Furthermore, one can show that the limit cycle becomes unstable at $\gamma_c \cong 2.8$ and is replaced by a multistable steady state for $\gamma > \gamma_c$ (corresponding to the 4 stable steady states of the combined reaction steps (62b) and (62c) which are dominant in this region). But a detailed discussion of that kind of non-equilibrium phase transition is beyond the scope of this paper and, hence, we restrict ourselves to values of γ smaller than γ_c.

In order to get differential equations which can be treated by simple analysis, but still give a rough sketch of the limit cycle behaviour obtained in Fig. 7, we replace q_x in the brackets of Eq. (65a) as well as q_y in Eq. (65b) by $r =_{\mathrm{Def}} \sqrt{q_x{}^2 + q_y{}^2}$. As we shall see at once, this implies that the real limit cycle is approximated by a circle of radius Δ, and the real propagation velocity along the limit cycle, $v_\parallel(\varphi)$, by the isotropic oscillation velocity $\omega \Delta$ (see Figure 8). When introducing the generalized coordinates $q_+ = q_x + i q_y$ and $q_- = q_x - i q_y$, the two coupled differential equations decouple into independent equations for the modes q_+ and q_-,

$$\frac{\mathrm{d}}{\mathrm{d}t} q_+ = (i\,\omega - \alpha_c)\, q_+ - k_c\, |q_+|^2\, q_+ , \tag{66a}$$

$$\frac{\mathrm{d}}{\mathrm{d}t} q_- = (-\,i\,\omega - \alpha_c)\, q_- - k_c\, |q_-|^2\, q_- , \tag{66b}$$

with

$$\alpha_c = -\,k_c\,\Delta^2, \quad r = |q_+| \overset{!}{=} |q_-| .$$

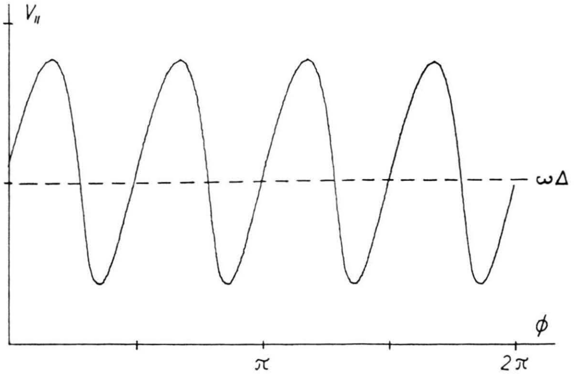

Fig. 8. The propagation velocity along the $\gamma = 2.0$-limit cycle of Fig. 7 is shown as a function of the phase $\varphi = \arctan q_y/q_x$.

These equations are easily solved by the Ansätze

$$q_+ = r\,e^{+i\omega t} \quad \text{and} \quad q_- = r\,e^{-i\omega t} \tag{67a}$$

so that we remain with the differential equation

$$\frac{\mathrm{d}}{\mathrm{d}t}\, r = k_c (\Delta^2 - r^2)\, r , \tag{67b}$$

determining the relaxation of r to its stationary solution $r_0 = \Delta$. Here, the quantity r measures the distance of the concentration oscillation from the center, $q_x = q_y = 0$, which now has become an unstable focus.

Summarizing the considerations above, we can state:

i) The period of the concentration oscillation, $T = 2\pi\omega^{-1}$ is essentially proportional to the inverse parameter of the reaction steps giving rise to conservative oscillations, k_{LV}^{-1}.

ii) The limit cycle comes into being because of reaction steps showing bistability (trimolecular reactions!), and the diameter of this cycle, in first approximation, is equal to the distance between the corresponding stable steady states.

iii) The time necessary for the concentration oscillation to approach the limit cycle, scales with the inverse parameter of the bistable reaction steps, k_c^{-1}.

To make the considerations complete, we finally show how the limit cycle originates from a simple initial steady state by a non-equilibrium phase transition. Above the "critical points" of the reaction steps (62b), (62c) (cf. Chapt. III), the quantity $\alpha_c = -\,k_c \Delta^2$ has positive values. Thus we can linearize Eqs. (66) which already have the form usual in generalized time-dependent Landau theory [4], and for the modes (order parameters) q_+ and q_-, we get solutions relaxing as

$$q_{+,\,\mathrm{lin}} \sim e^{-(\alpha_c - i\omega)t}\,, \quad q_{-,\,\mathrm{lin}} \sim e^{-(\alpha_c + i\omega)t}\,. \tag{68}$$

In the regime $\alpha_c > 0$, the center, $q_x = q_y = 0$, therefore is a stable focus and no limit cycle can exist. But if the reaction steps (62b), (62c) approach their critical points, with α_c going to zero, that focus becomes unstable. Since ω remains at positive values all the time, this instability (hence called a hard-mode instability) then gives birth to a limit cycle.

V.2. Irreversible Circulation of Fluctuations, Orbital Revolution, and Dephasing

In addition to the deterministic description of the preceding section, again, we have to include concentration fluctuations. For this purpose, firstly, we extend the formalism of stochastics reviewed in Chapt. II to two degrees of freedom. Because of the reaction step $X + Y \rightarrow 2\,Y$, the master equation [cf. Eq. (12)] now contains not only transitions belonging to creation or annihilation of one molecule of either the X- or the Y-substance, but also transitions combining the creation of one Y-molecule with annihilation of one X-molecule. Therefore, in generalization of Eq. (12), we get

$$\begin{aligned}\frac{\partial}{\partial t}\, p(n_x, n_y; t) = {} & - V\{R_{+X} + R_{-X} + R_{+Y} + R_{-Y} + R_{-X,+Y}\}\big|_{x=n_x/V,\, y=n_y/V} \cdot p(n_x, n_y; t) \\ & + V\{R_{-X}\big|_{x=(n_x+1)/V,\, y=n_y/V} \cdot p(n_x + 1, n_y; t) + R_{+X}\big|_{x=(n_x-1)/V,\, y=n_y/V} \\ & \cdot p(n_x - 1, n_y; t) + R_{-Y}\big|_{x=n_x/V,\, y=(n_y+1)V} \cdot p(n_x, n_y + 1; t) + R_{+Y}\big|_{x=n_x/V,\, y=(n_y-1)/V} \\ & \cdot p(n_x, n_y - 1; t) + R_{-X,+Y}\big|_{x=(n_x+1)/V,\, y=(n_y-1)/V} \cdot p(n_x + 1, n_y - 1; t)\}\,.\end{aligned} \tag{69}$$

Returning to the variables x, y and expanding the master equation in the same manner as was done for evaluating Eq. (18), we obtain the Fokker-Planck equation

$$\begin{aligned}\frac{\partial}{\partial t}\,\varrho(x, y; t) = {} & -\frac{\partial}{\partial x}\{v_x(x, y)\,\varrho(x, y; t)\} \\ & -\frac{\partial}{\partial y}\{v_y(x, y)\,\varrho(x, y; t)\} \\ & + \frac{1}{V}\left\{\frac{\partial^2}{\partial x^2}(D_x(x, y)\,\varrho) + \frac{\partial^2}{\partial y^2}(D_y(x, y)\,\varrho)\right. \\ & \left. - \frac{\partial^2}{\partial x\,\partial y}(R_{-X,+Y}(x, y)\,\varrho(x, y; t))\right\}\end{aligned} \tag{70}$$

with

$$\begin{aligned} v_x &= R_{+X} - R_{-X} - R_{-X,+Y}\,, \\ v_y &= R_{+Y} - R_{-Y} + R_{-X,+Y}\,, \\ D_x &= \tfrac{1}{2}(R_{+X} + R_{-X} + R_{-X,+Y})\,, \\ D_y &= \tfrac{1}{2}(R_{+Y} + R_{-Y} + R_{-X,+Y})\,. \end{aligned}$$

α) Moment Equations Above the Phase Transition Point

As in Sect. III.2, also here, it is not sufficient to use the system size expansion for the calculation of the moments of $\varrho(x, y; t)$ because then we would get variances diverging at the critical point [26], thus making the introduced information measures collapse. Therefore, we have to derive the moment equations directly from the Fokker-Planck equation (70):

$$\begin{aligned}\frac{\partial}{\partial t}\langle x^\nu y^\mu\rangle &= \int_0^1\!\!\int_0^1 x^\nu y^\mu \frac{\partial}{\partial t}\,\varrho(x, y; t)\,\mathrm{d}x\,\mathrm{d}y \\ &= \nu\,\langle x^{\nu-1} y^\mu v_x\rangle + \mu\,\langle x^\nu y^{\mu-1} v_y\rangle \\ & + \frac{1}{V}\{\nu(\nu-1)\,\langle x^{\nu-2} y^\mu D_x\rangle + \mu(\mu-1) \\ & \cdot \langle x^\nu y^{\mu-2} D_y\rangle - \nu\,\mu\,\langle x^{\nu-1} y^{\mu-1} R_{+X,-Y}\rangle\}\end{aligned} \tag{71}$$

Transforming to the variables q_x, q_y so that $v_x(q_x, q_y)$ and $v_y(q_x, q_y)$ become identical to the right-hand sides of Eqs. (65a) and (65b), replacing the functions

$$D_x(q_x, q_y), \quad D_y(q_x, q_y), \quad \text{and} \quad R_{-X,+Y}(q_x, q_y)$$

by their values at $q_x = q_y = 0$,

$$\begin{aligned} D_x = D_y &= k_{\mathrm{LV}}\, x_0{}^2 + k_{\mathrm{c}}\, D =_{\mathrm{Def}} D_{\mathrm{c}}\,, \\ R_{-X,+Y} &= k_{\mathrm{LV}}\, x_0{}^2\,, \end{aligned} \tag{72}$$

where D is the constant already introduced in Sect. III.2 (see Eqs. (44)), and closing up the hierarchy of the moment equations by assuming the probability distribution $\varrho(q_x, q_y; t)$ to be of Gaussian form

$$\begin{aligned}\varrho(\underline{q}; t) = {} & \frac{V}{2\pi}\sqrt{\det g(t)} \\ & \exp\left\{-\frac{V}{2}(\underline{q} - \langle\underline{q}\rangle)^{\mathrm{T}} g(t)\,(\underline{q} - \langle\underline{q}\rangle)\right\}\end{aligned} \tag{73}$$

with $\underline{q} =_{\text{Def}} \begin{pmatrix} q_x \\ q_y \end{pmatrix}, \quad g(t) = \begin{pmatrix} g_{xx} & g_{xy} \\ g_{xy} & g_{yy} \end{pmatrix},$

where $g(t)$ is the inverse of the variance matrix $\sigma(t)$, after some algebra, we finally get the differential equations

$$\begin{aligned}
\frac{\mathrm{d}}{\mathrm{d}t}\bar{q}_x &= -\omega\,\bar{q}_y - \left(\alpha_c + \frac{3k_c}{V}\sigma_{xx}\right)\bar{q}_x - k_c\,\bar{q}_x^3\,,\\
\frac{\mathrm{d}}{\mathrm{d}t}\bar{q}_y &= \omega\,\bar{q}_x - \left(\alpha_c + \frac{3k_c}{V}\sigma_{yy}\right)\bar{q}_y - k_c\,\bar{q}_y^3\,,\\
\frac{\mathrm{d}}{\mathrm{d}t}\sigma_{xx} &= -2\omega\,\sigma_{xy} - 2(\alpha_c + 3k_c\,\bar{q}_x^2)\,\sigma_{xx}\\
&\quad - \frac{6k_c}{V}\sigma_{xx}^2 + 2D_c\,,\\
\frac{\mathrm{d}}{\mathrm{d}t}\sigma_{yy} &= 2\omega\,\sigma_{xy} - 2(\alpha_c + 3k_c\,\bar{q}_y^2)\,\sigma_{yy} \qquad (74)\\
&\quad - \frac{6k_c}{V}\sigma_{yy}^2 + 2D_c\,,\\
\frac{\mathrm{d}}{\mathrm{d}t}\sigma_{xy} &= \omega(\sigma_{xx} - \sigma_{yy})\\
&\quad - \left\{2\alpha_c + 3k_c(\bar{q}_x^2 + \bar{q}_y^2) + \frac{3k_c}{V}(\sigma_{xx} + \sigma_{yy})\right\}\\
&\quad \cdot\sigma_{xy} - R_{-X,+Y}\,,
\end{aligned}$$

($\alpha_c = -k_c\Delta^2$). These coupled non-linear differential equations describe the concentration fluctuations around the focus, $q_x = q_y = 0$, which is stable within the phase considered here. By the reaction steps responsible for the concentration oscillations, these fluctuations are induced to show some kind of circulating behaviour [26] which, in turn, is just the reason for the coupling between the x- and y-components of the mean and the variance. Although we content ourselves with the simplest approximation just guaranteeing a non-absurd result at the critical (phase transition) point, viz., we take only those parts of the fluctuations into account which are of Gaussian form, the mathematics have already become complicated, as is demonstrated by the Equations (74).

Here, we will not go into detailed calculations, but make only two comments. Together with

$$\lim_{t\to\infty}\bar{q}_x(t) = \lim_{t\to\infty}\bar{q}_y(t) = 0\,,$$

we can estimate the limiting values of the variance matrix by

$$-D_c/\omega \leqq \sigma_{xy}(\infty) \leqq +D_c/\omega\,, \qquad (75\text{a})$$

$$\sqrt{\tfrac{1}{2}(\sigma_{xx}^2(\infty) + \sigma_{yy}^2(\infty))} \leqq \sqrt{\tfrac{1}{3}V D_c/k_c}\,, \qquad (75\text{b})$$

where the latter becomes an equality at the critical point. Comparing (75b) with the critical variance due only to the reaction steps giving a phase transition towards bistability (see Eq. (**46**)), because of $D_c/k_c > D$ (see Eq. (72)), we find that the average variance per degree of freedom is increased in the combined system treated here. For the limit of vanishing competition between oscillation and the reaction steps (62b, c), $k_c \to 0$, the variance diverges and thus indicates some kind of chaotic behaviour characteristic for the fluctuations of the oscillating Lotka-Volterra reaction itself [3]. The time scale on which the probability distribution $\varrho(q_x, q_y; t)$ approaches the stationary (limiting) distribution is proportional to α_c^{-1} if the system is outside of its critical region. Within that region that time scale is proportional to $\sqrt{V/(D_c k_c)}$ In accordance with the argument above, for every fixed distance from the critical point this time scale also increases with decreasing competition strength, k_c.

β) Rough Approximation within the Limit Cycle Regime

In the region below the phase transition, the concentration fluctuations around and along the limit cycle give rise to a probability distribution of a form like a dike which covers a section of that cycle. Therefore, a Gaussian distribution dependent on the coordinates q_x, q_y is unsuitable for an approximative procedure within this regime. To have a simple symmetry, we again replace the actual limit cycle by a circle, i.e., we set

$$\begin{aligned}
v_x &= -\omega\,q_y + k_c(\Delta^2 - r^2)\,q_x\,, \qquad (76)\\
v_y &= \omega\,q_x + k_c(\Delta^2 - r^2)\,q_y\,, \quad r = \sqrt{q_x^2 + q_y^2}\,.
\end{aligned}$$

For the same reason, we drop the mixed second derivative term of the Fokker-Planck equation (70) because this term prevents an isotropic solution for the stationary probability distribution, as can be seen from Equations (74). (For $R_{-X,+Y} \equiv 0$, Eqs. (74) result in $\sigma_{xx}(\infty) = \sigma_{yy}(\infty)$, $\sigma_{xy}(\infty) = 0$!) Again replacing $D_x(x, y)$ and $D_y(x, y)$ by D_c, we now can easily transform the Fokker-Planck equation to polar coordinates ($q_y/q_x =_{\text{Def}} \tan\varphi$ and r as defined above!):

$$\frac{\partial}{\partial t}\varrho(r,\varphi;t) = -\frac{1}{r}\frac{\partial}{\partial r}(r\,v_r\,\varrho) - \frac{1}{r}\frac{\partial}{\partial\varphi}(v_\varphi\,\varrho) \qquad (77)$$
$$+ \frac{D_c}{V}\left\{\frac{1}{r}\frac{\partial}{\partial r}\left(r\frac{\partial}{\partial r}\varrho\right) + \frac{1}{r^2}\frac{\partial^2}{\partial\varphi^2}\varrho\right\}$$

with

$$v_r(r,\varphi) = v_x\cos\varphi + v_y\sin\varphi = k_c(\Delta^2 - r^2)\,r\,,$$
$$v_\varphi(r,\varphi) = -\,v_x\sin\varphi + v_y\cos\varphi = \omega\,r\,.$$

If the reaction system is outside of its very critical region ($\Delta^2 \gg \sqrt{D_c/(k_c V)}$!), i.e., if the concentration fluctuations are already strongly localized around the limit cycle, in Eq. (77), we can approximately replace r by the radius of the cycle, Δ, and v_r which is zero at $r=\Delta$, by the first derivative term of its Taylor expansion around $r=\Delta$, $v_r \cong -2k_c\Delta^2 q_r$ with $q_r =_{\text{Def}} r-\Delta$*. In this approximation, the Fokker-Planck equation is solved by the product-form distribution $\varrho(r,\varphi;t) = \varrho_r(q_r;t)\cdot\varrho_\varphi(\varphi;t)$ where ϱ_r and ϱ_φ are governed by

$$\frac{\partial}{\partial t}\varrho_r(q_r;t) = 2k_c\Delta^2\frac{\partial}{\partial q_r}(q_r\,\varrho_r) + \frac{D_c}{V}\frac{\partial^2}{\partial q_r{}^2}\varrho_r\,, \tag{77a}$$

$$\frac{\partial}{\partial t}\varrho_\varphi(\varphi;t) = -\,\omega\frac{\partial}{\partial\varphi}\varrho_\varphi + \frac{D_c}{V\Delta^2}\frac{\partial^2}{\partial\varphi^2}\varrho_\varphi\,. \tag{77b}$$

Quite analogously to Eq. (20), both differential equations have Gaussian solutions. The first and second moments of ϱ_r and ϱ_φ are given by

$$\frac{d}{dt}\bar q_r = -\,2k_c\Delta^2\bar q_r \quad \left(\bar q_r \overset{!}{=} \int_0^\infty r\,\varrho_r(q_r;t)\,dr - \Delta\right), \tag{78a}$$

$$\frac{d}{dt}\sigma_r = -\,4k_c\Delta^2\sigma_r + 2D_c\,; \tag{78b}$$

$$\frac{d}{dt}\bar\varphi = \omega, \quad \frac{d}{dt}\sigma_\varphi = 2\frac{D_c}{\Delta^2}\,. \tag{79}$$

(Here, we used again $V^{-1}\sigma_r = \langle(q_r-\bar q_r)^2\rangle$, $V^{-1}\sigma_\varphi = \langle(\varphi-\bar\varphi)^2\rangle$!)

The fluctuation stochastics *perpendicular* to the limit cycle (represented by Eqs. (78)) are of the same kind as those around the steady state x_0 discussed in Chapt. II or the fluctuations around the two steady states $x_{s,+}$ and $x_{s,-}$ of the bistable reaction system presented in Chapt. III in the case of that system being below its phase transition and already well separated from the critical region. Therefore, we can restrict ourselves to the statement that the time necessary for $\varrho_r(q_r;t)$ to relax into its stationary limiting distribution $\varrho_{r,\infty}(q_r)$ scales as $(k_c\Delta^2)^{-1}$ (cf. Section III.2.γ).

The stochastics *along* the limit cycle, however, are of a quite different type. According to the concentration oscillation found within deterministic reaction kinetics (cf. Eq. (67a)), the mean value of $\varrho_\varphi(\varphi;t)$ moves along the φ-coordinate with constant velocity ω (called the orbital revolution). On the other hand, the variance increases linearly in time. This means: if the reaction system starts at time t_0 at $\varphi(t_0)$ then the phase at later times is not sharply determined by $\varphi(t) = \omega(t-t_0) + \varphi(t_0)$, as predicted by the deterministic theory, but has a Gaussian probability distribution around that value which spreads out more and more as time goes on. Thus the microscopic concentration fluctuations cause a dephasing of the macroscopic concentration oscillation.

In view of the "information measures" introduced which shall be applied also here, we have to ask for the stationary probability distribution. As has already become apparent from the arguments above and from Eqs. (79), for $\varrho_\varphi(\varphi;t)$ no limiting distribution can be defined. This problem is not present if we are not interested in the absolute phase φ, but only in the position of the reaction system within the x-y-diagram:

$$\Phi =_{\text{Def}} \arctan q_y/q_x \quad \text{with} \quad -\pi < \Phi \leqq \pi \tag{80}$$
$$\Leftrightarrow\ \Phi =_{\text{Def}} \varphi \ \text{modulo}\ 2\pi\,.$$

The probability distribution for this "modulo-2π-reduced" variable is given by

$$\varrho_\Phi(\Phi;t) = \sum_{\nu=-\infty}^{+\infty}\varrho_\varphi(\varphi + 2\pi\nu\,;t)\,, \tag{81}$$

and one can show that this distribution tends to $\varrho_{\Phi,\infty}(\Phi) = 1/2\pi$ for $t\to\infty$, i.e., to an equipartition along the limit cycle. Since the corresponding limiting value of the variance is equal to $V^{-1}\sigma_{\Phi,\infty} = \frac{1}{3}\pi^2$, by comparison with Eq. (79), we find that the time necessary for the relaxation of $\varrho_\Phi(\Phi;t)$ scales with $V\Delta^2/D_c$.

As a last point, we remark that the stationary probability distribution found here is not compatible with the usual "condition of detailed balance" [26]. The limiting distribution along the limit cycle, $\varrho_{\Phi,\infty}(\Phi)$, rather fulfills the condition

$$\int d\Phi'\{w_{\Phi'\to\Phi}\,\varrho_{\Phi,\infty}(\Phi') - w_{\Phi\to\Phi'}\,\varrho_{\Phi,\infty}(\Phi)\} = \omega/2\pi \tag{82}$$

For $\omega = 0$, this equation would be simply a generalized (continuous!) version of the detailed balance

---

* For an expansion developed for the very critical region by using scaling-theory arguments, see [52, 53, 54].

condition (14). But for $\omega \neq 0$, that balance of "probability mass flow" is replaced by an effective overall "probability mass flow" which just corresponds to the orbital revolution of the limit cycle system. (This behaviour is also present in the probabilistic description of one-dimensional disordered systems as, e.g., electrons in an amorphous material [47].)

V.3. Conservation of Information

As was already the case for the reaction system treated in Chapt. III, also here the phase below the critical point will be the only one giving rise to quasi conservation of information. Since the probability distribution $\varrho(x, y; t)$, in this regime, can be written approximately as a product of a radial part $\varrho_r(q_r; t)$ and an orbital part $\varrho_\Phi(\Phi; t)$, the information measures $J(\tau/\varrho_\infty)$ and $J(\tau/\varrho_\infty; t-t_*)$ split up each into a sum of a radial and an orbital contribution:

$$J(\tau/\varrho_\infty) = J_r(\tau/\varrho_{r,\infty}) + J_\Phi(\tau/\varrho_{\Phi,\infty})\,, \tag{83a}$$

$$J(\tau/\varrho_\infty; t-t_*) = J_r(\tau/\varrho_{r,\infty}; t-t_*) + J_\Phi(\tau/\varrho_{\Phi,\infty}; t-t_*)\,. \tag{83b}$$

This separation is a direct consequence of the information gain property

$$K(\varrho_\nu\, \varrho_\mu/\varrho_\nu'\, \varrho_\mu') = K(\varrho_\nu/\varrho_\nu') + K(\varrho_\mu/\varrho_\mu')\,,$$

as can be shown immediately (cf. Eqs. (6), (7), (32)).

The radial contributions can be estimated by the results of Sect. III.3 because, as was pointed out in the preceding section, the concentration fluctuations perpendicular to the limit cycle behave as those around one of the steady states of the bistable reaction system, or, what amounts to essentially the same (exept of a factor of 2 in the differential equations for the mean value and the variance of the probability distribution), as those around the single steady state in the upper phase of the reaction scheme (36): As functions of the limit cycle radius Δ, $J_r(\tau/\varrho_{r,\infty})$ and $J_r(\tau/\varrho_{r,\infty}; t-t_*)$ approximately have the same shape as the $b > b_c$ parts of $J(\tilde\tau/\varrho_\infty)$ and $J(\tilde\tau/\varrho_\infty; \tilde t - \tilde t_*)$ drawn in Figs. 4 and 5, if we connect the parameter b and Δ by $b - b_c = k_c \Delta^2$ (cf. Eq. (39)) and the scales of t and $\tilde t$ by $\tilde t = k_c t$ [in Chapt. III, we chose a time scale such that $k_c = k_{\leftarrow}^{(1)}$ became equal to unity (cf. Eq. (43))!]. Therefore, the radial part of the fluctuations does not contribute to a quasi conservation of information, except if we define quasi conservation on a time scale much smaller than the radial relaxation time, $(k_c \Delta^2)^{-1}$, which in turn, is much smaller than the scale of the critical relaxation, $\sqrt{V/(k_c D_c)}$. (The very critical region, $\Delta^2 \lesssim \sqrt{D_c/(k_c V)}$, is excluded from our considerations here because, there, the above separation of the probability distribution is no longer possible anyhow.)

In order to clear of the information measures from fast relaxing parts of the fluctuations, we assume the time interval necessary for the measurement of the detector to be of a length τ comparable to the critical relaxation time ($\tau \simeq \sqrt{V/(k_c D_c)}$). For this τ, the radial contributions $J_r(\tau/\varrho_{r,\infty})$ and $J_r(\tau/\varrho_{r,\infty}; t-t_*)$ become totally negligible for all Δ-values outside the very critical region so that the information measures now are determined solely by the fluctuations along the limit cycle. The calculation of the expressions $J_\Phi(\tau/\varrho_{\Phi,\infty})$ and $J_\Phi(\tau/\varrho_{\Phi,\infty}; t-t_*)$, however, can not be done in exactly the same manner as in Sects. II.4, II.5 and also III.3, because the time dependence of the variable Φ consists of the macroscopic orbital revolution *and* the microscopic fluctuations around that macroscopic movement: A detector which measures by the same procedure of averaging as indicated by Eq. (28), would give outputs almost equal to $\varrho_{\Phi,\infty}(\Phi)$ whenever the period of the concentration oscillation, $T = 2\pi/\omega$, is smaller than the duration of the measurement, τ. If we want to get an experimental access to the real fluctuations along the limit cycle, the detector rather must be able to compensate for the macroscopic movement (which is totally determined by "deterministic" laws!). Mathematically, this means that the detector measures probability distributions not in the fixed $q_x - q_y$-frame, but rather in a $q_x' - q_y'$-frame which rotates with the same angular velocity ω as the deterministic concentration oscillations do:

$$q_x' = q_x \cos\omega(t-t_0) + q_y \sin\omega(t-t_0)\,,$$

$$q_y' = -\,q_x \sin\omega(t-t_0) + q_y \cos\omega(t-t_0)\,.$$

In this rotating frame, the angular phase of the reaction system, Φ', fluctuates around a *fixed* mean value $\overline{\Phi'} = \Phi(t_0)$ whereas the variance of the corresponding probability distribution $\varrho_{\Phi'}(\Phi'; t)$ increases again linearly in time as already indicated by the second equation of (79). Quite analogously to Eq. (28), the detector measurement during the time interval $t_0 < t < t_0 + \tau$ will then result in

$$\varrho_{\Phi',\text{detect}}(\Phi'/\Phi(t_0)) = \frac{1}{\tau}\int_{t_0}^{t_0+\tau} \tilde\varrho_{\Phi'}(\Phi'; t)\,\mathrm{d}t \tag{84}$$

where the distribution $\tilde{\varrho}_{\Phi'}(\Phi'; t)$ is fixed by the initial condition

$$\tilde{\varrho}_{\Phi'}(\Phi'; t_0) = \delta(\Phi' - \Phi(t_0)) .$$

Now doing the further calculations in the spirit of Sects. II.4 and II.5, we finally get

$$J\left(\tau = \sqrt{\frac{V}{k_c D_c}} / \varrho_\infty\right) \simeq \frac{1}{2} \operatorname{ld}\left(\pi \Delta^2 \sqrt{\frac{k_c V}{D_c}}\right), \tag{85a}$$

$$J\left(\tau = \sqrt{\frac{V}{k_c D_c}} / \varrho_\infty ; t - t_*\right) \simeq J(\tau/\varrho_\infty) \tag{85b}$$

$$- \left\{\frac{1}{2} \operatorname{ld}\left(1 + 2\frac{t - t_*}{\tau}\right) - \frac{t - t_*}{\tau + 2(t - t_*)}\right\} .$$

Here, the latter line is an estimate of $J(\tau/\varrho_\infty; t - t_*)$ only valid for durations $t - t_*$ within which the distributions $\tilde{\varrho}_{\Phi'}(\Phi'; t)$ may still be approximated by Gaussian forms. (As follows from Eq. (81), $\tilde{\varrho}_{\Phi'}(\Phi'; t)$ deviates more and more from a Gaussian distribution when approaching its stationary distribution $\tilde{\varrho}_{\Phi', \infty}(\Phi') = 1/2\pi$, i.e., when $t - t_*$ reaches the order of the relaxation time of $\tilde{\varrho}_{\Phi'}(\Phi'; t)$, viz., $V\Delta^2/D_c$!)

Summarizing the above considerations, we can state:

i) The average amount of information one gets by doing a measurement increases logarithmically with the diameter of the limit cycle, i.e., with increasing distance from the phase transition point.

ii) The averaged amount of the information being stored within the reaction system essentially also decays logarithmically with increasing storage time.

Contrary to the bistable reaction system of Chapt. III, for which we obtained a distinct separation between the fast and the slow relaxation processes, and were thus led to a natural way of defining quasi conservation of information, the limit cycle system considered here does not have such a sharp separation between different time scales, because the "diffusion process" along the limit cycle which represents the more slowly relaxing parts of the concentration fluctuations, in turn, consists of a whole spectrum of more or less slow relaxation processes: According to Eq. (85b), a large amount of information can be conserved only for a relatively short time, whereas a smaller amount can be stored for a longer time. Therefore, we may define time scales for quasi conservation by asking: "How long is the limit cycle system able to store a certain amount of information?" From Eq. (85b) we find that the amount of just ν "bits" can be stored during a time interval of length

$$\Delta T_\nu \simeq 2^{-2\nu} \cdot \Delta^2 V / D_c . \tag{86}$$

In this formula, the factor $\Delta^2 V/D_c$ is just the time scale corresponding to the decay of *all* of the stored information.

V.4. Embedding into a Network

As we did in Chapt. IV, also here, we may ask whether a system of limit cycles is suited to work as an information pump within a chemical network. To be concrete from the beginning, we consider the following situation (cf. Fig. 9): The reaction volume is divided into two parts by a semipermeable membrane which is impermeable only to the intermediate reaction partners of the reaction scheme (62), X and Y. By this, in both parts of the volume, concentration oscillations can occure independently from each other. Via the catalytic reaction steps

$$I \underset{X}{\rightarrow} Z , \quad Z \rightarrow I , \tag{87a}$$

$$J \underset{2Z}{\rightarrow} H , \quad H \rightarrow J , \tag{87b}$$

the X-concentrations within these volume parts, x_1 and x_2, then are assumed to regulate the production rate of the synthesis process

$$\mathrm{C} + \mathrm{D} \underset{\mathrm{H}}{\rightarrow} F . \tag{88}$$

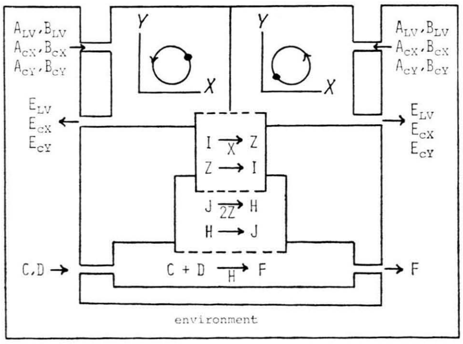

Fig. 9. This chemical network contains two identical reaction systems with oscillating behaviour as "information generators". Again, it should be stated that the reaction steps noted above generally do not represent real chemical reactions, but have the meaning of shortened forms in the same sense as has been mentioned below Figure 6.

If the reaction steps (87a) depend on the X-concentration very sensitively, i.e., if the relaxation time of these reaction steps is much smaller than the period of the X-concentration oscillation, $k_{\mathrm{I}\to\mathrm{Z}}^{-1}, k_{\mathrm{Z}\to\mathrm{I}}^{-1} \ll T = 2\pi/\omega$, by

$$x_1(t) = x_0 + \Delta \cos(\omega t + \Phi_{0,1}) \quad \text{and}$$
$$x_2(t) = x_0 + \Delta \cos(\omega t + \Phi_{0,2})$$

the Z-concentration is induced to also perform oscillations with the same period T, but with an amplitude which is proportional to the cosine of half the difference between the phases of x_1 and x_2: for $x_1(t) = x_2(t)$ ($\triangleq \Phi_{0,1} - \Phi_{0,2} = 0$) the amplitude is maximal, whereas it vanishes for $x_1(t) = -x_2(t)$ ($\triangleq |\Phi_{0,1} - \Phi_{0,2}| = \pi$). In order to have a smooth production rate of the synthesis (88) even in the regime where the "information pump" (62) shows its critical behaviour, as was already necessary for the network discussed in Chapt. IV, also here, the synthesis process must be coupled to the "information pump" by slow reaction steps which have relaxation times comparable to the critical relaxation time of the limit cycle system, i.e., $k_{\mathrm{J}\to\mathrm{H}}^{-1}$, $k_{\mathrm{H}\to\mathrm{J}}^{-1}$ must beof order $\sqrt{V/(D_c k_c)}$. In this case and for an oscillation period $T \ll \sqrt{V/(D_c k_c)}$, the reaction steps (87b) work as a network element which integrates over the z-oscillation, so that the H-concentration becomes a constant value. Since the rate equation corresponding to Eqs. (87b) depends on z quadratically, the value of h is a function of the amplitude of $z(t)$ and, hence, of the phase difference between the two limit cycles on both sides of the membrane. By this, the production rate of the synthesis process indeed varies according to the information given into the chemical network by the limit cycle elements. Contrary to the network of Chapt. IV, the network system considered here is *not* able to utilize *all* the information given by the "information pumps". The reason is that the absolute phase of each of the two limit cycle elements is of no meaning for the production rate of (88), rather only the difference between the two phases is. Thus the amount of information connected to knowledge about the absolute phases is wiped out within the network so that only the information contribution due to the phase *difference* is of value.

VI. Successive Phase Transitions to Multistable Steady States

The non-equilibrium phase transitions discussed in this paper up to here have in common that they are induced by reaction steps giving rise to bistable steady states (cf. Chapts. III and V!). Now it is quite natural to ask what is necessary to obtain further bifurcations of the bistable steady state towards multistable steady states. We shall answer this question only very shortly and, for this purpose, we restrict ourselves to a one-component reaction system and treat it mathematically in its most symmetrical situation.

VI.1. Construction of a One-Component Reaction Scheme

In the framework of deterministic reaction kinetics, the right-hand side of a rate equation, $\mathrm{d}x/\mathrm{d}t = v(x)$, which describes a one-component reaction system showing four stable steady states, must have four zero points at which its first derivative has negative values:

$$v(x)\Big|_{x=x_{s,\nu}} = 0\,; \quad \frac{\mathrm{d}}{\mathrm{d}t}\, v(x)\Big|_{x=x_{s,\nu}} < 0\,, \qquad \nu = 1, 2, 3, 4\,. \tag{89}$$

In order to guarantee that the reaction system approaches one of these steady states for every initial concentration $x(t_0)$ possible, $v(x)$ must be positive for all x-values smaller than the minimal $x_{s,\nu}$ and negative for all x-values greater than the maximal $x_{s,\nu}$. This and Eq. (89) require that $v(x)$ must have additionally just three zero points, $x_{u,\nu}$, $\nu = 1, 2, 3$, at which $\mathrm{d}v(x)/\mathrm{d}t$ has positive values. For the sake of simplicity, we assume $v(x)$ to have the following symmetric "zero point constellation"

$$v(x) = -g \cdot \prod_{\nu=1}^{3} (x - x_{s,\nu})(x - x_{u,\nu}) \cdot (x - x_{s,4}) \tag{90}$$

with

$$x_{u,1} = x_0 - \Delta\,, \qquad x_{u,2} = x_0\,,$$
$$x_{u,3} = x_0 + \Delta\,,$$
$$x_{s,1} = x_{u,1} - \delta\,, \qquad x_{s,2} = x_{u,1} + \delta\,,$$
$$x_{s,3} = x_{u,3} - \delta\,, \qquad x_{s,4} = x_{u,3} + \delta \quad \text{and}$$
$$\Delta > \delta\,.$$

Generally, the prefactor g can be a function of x, Δ, and δ, that is positive everywhere and that at most can have zero points at the zero points of $v(x)$, $x_{s,\nu}$, $x_{u,\nu}$, already present. Here, we assume g to be independent of the x-variable. Evaluating the product, we then get a polynomial of seventh order within which, in the region of small Δ and δ-values, the coefficients change sign from one order in x to the next: the even x-power terms are positive and the odd ones are negative.

This form of the rate equation corresponds to the reaction scheme

$$A + 2X \underset{k^{(1)}_{\leftarrow}}{\overset{k^{(1)}_{\rightarrow}}{\rightleftarrows}} 3X\,, \tag{91.1}$$

$$A + 4X \underset{k^{(2)}_{\leftarrow}}{\overset{k^{(2)}_{\rightarrow}}{\rightleftarrows}} 5X\,, \tag{91.2}$$

$$A + 6X \underset{k^{(3)}_{\leftarrow}}{\overset{k^{(3)}_{\rightarrow}}{\rightleftarrows}} 7X\,, \tag{91.3}$$

$$B + \;\; X \underset{k^{(4)}_{\leftarrow}}{\overset{k^{(4)}_{\rightarrow}}{\rightleftarrows}} E\,, \tag{91.4}$$

because here the rates for the increase and the decrease of the X-concentration are given by

$$R_{+X} = k^{(4)}_{\leftarrow}\, e + a\,(k^{(1)}_{\rightarrow}\, x^2 + k^{(2)}_{\rightarrow}\, x^4 + k^{(3)}_{\rightarrow}\, x^6)\,, \tag{92a}$$

$$R_{-X} = k^{(4)}_{\rightarrow}\, b\, x + k^{(1)}_{\leftarrow}\, x^3 + k^{(2)}_{\leftarrow}\, x^5 + k^{(3)}_{\leftarrow}\, x^7\,, \tag{92b}$$

so that $v(x) = R_{+X} - R_{-X}$ has the property quoted above. The zero point parameters x_0, Δ, and δ are connected to the reaction parameters k and the concentrations of the initial and the final substances by the following equations:

$$\begin{aligned}
a\, k^{(1)}_{\rightarrow} &= g\,\{21\, x_0{}^5 - 10\,(3\,\Delta^2 + 2\,\delta^2)\, x_0{}^3 \\
&\qquad + 3\,(3\,\Delta^4 + \delta^4)\, x_0\}\,, \\
k^{(1)}_{\leftarrow} &= g\,\{35\, x_0{}^4 - 10\,(3\,\Delta^2 + 2\,\delta^2)\, x_0{}^2 + 3\,\Delta^4 + \delta^4\}, \\
a\, k^{(2)}_{\rightarrow} &= g\,\{35\, x_0{}^3 - 5\,(3\,\Delta^2 + 2\,\delta^2)\, x_0\}\,, \\
k^{(2)}_{\leftarrow} &= g\,\{21\, x_0{}^2 - (3\,\Delta^2 + 2\,\delta^2)\}\,, \\
a\, k^{(3)}_{\rightarrow} &= 7\, x_0\, g\,, \\
k^{(3)}_{\leftarrow} &= g\,, \\
b\, k^{(4)}_{\rightarrow} &= g\,\{7\, x_0{}^6 - 5\,(3\,\Delta^2 + 2\,\delta^2)\, x_0{}^4 \\
&\qquad + 3\,(3\,\Delta^4 + \delta^4)\, x_0{}^2 - (\Delta^2 - \delta^2)^2\, \Delta^2\}, \\
e\, k^{(4)}_{\leftarrow} &= g\,\{x_0{}^7 - (3\,\Delta^2 + 2\,\delta^2)\, x_0{}^5 + (3\,\Delta^4 + \delta^4)\, x_0{}^3 \\
&\qquad - (\Delta^2 - \delta^2)^2\, \Delta^2\, x_0\}\,.
\end{aligned} \tag{93}$$

Since the x-powers of $v(x)$ have coefficients dependent not on Δ, δ, but rather on Δ^2, δ^2, non-equilibrium phase transitions of the reaction system (91) which are analogous to the second order transition of the Schlögl model treated in Chapt. III, come about in the same way as was discussed in Sect. III.1: Above the upper "critical point", Δ^2 *and* δ^2 are negative and, therefore, x_0 is the only real-valued zero point of $v(x)$, i.e., only the single steady state "$x = x_0$" exists in this regime. Below that "critical point", Δ^2 becomes positive so that now the stationary solutions $x_{u,1}$, $x_{u,3}$ indicate a bistable steady state. For a further bifurcation of the steady states, it is necessary that also δ^2 goes through zero to positive values. Below this second "critical point", $v(x)$ in fact has seven real-valued zero points (cf. Eq. (90)) and four of them, $x_{s,\nu}$, $\nu = 1, 2, 3, 4$, represent stable steady states.

VI.2. Stochastics and Information Content

Here, we omit a detailed calculation of the stochastics of the reaction system just outlined, because the basic features can be already deduced by simply generalizing the considerations of Sect. III.2: In the regime where $\Delta^2, \delta^2 < 0$, the probability distribution for the X-concentration, $\varrho(x; t)$, is localized around x_0. When going through the upper "critical point", $\varrho(x; t)$ spreads out (the variance enlarges and reaches values of the order $\sqrt{V}$) and then decomposes into a doubly peaked distribution characteristic for the $\Delta^2 > 0$; $\delta^2 < 0$-regime. As the system approaches the lower "critical point", each of the two peaks again spreads out (the variance of each peak becomes proportional to $\sqrt{V}$) and, beyond the second phase transition, once more decomposes into two peaks, so that $\varrho(x; t)$ is four-peaked in the $\Delta^2, \delta^2 > 0$-regime.

In order to get contact with the information formulae, it is necessary to know also the relative statistical weights the single peaks have within the total distribution $\varrho(x; t)$, which are given each by the area covered by (i.e., the integral over) the corresponding peak. As was already the case along the coexistence-line of the reaction system (36), in the region of bistability, the two peaks of the stationary (limiting) distribution $\varrho_\infty(x)$ have the same statistical weight (cf. Sect. III.2.β below Eqs. (55)). This, however, is not true for the *four* peaks of $\varrho_\infty(x)$ within the "lowest" phase. From the Fokker-Planck approximation of the limiting distribution [4], $\varrho_\infty(x) \sim \exp\{-\int^{x} v(x')\,\mathrm{d}x'/(V^{-1}D)\}$, one immediately can show that the statistical weights of the outer peaks (placed around $x_{s,1}$ and $x_{s,4}$) are in general much greater than those of the inner peaks. (Because of the inversion symmetry of $\int^{x} v(x)'\,\mathrm{d}x'$ with respect to $x = x_0$, both the outer peaks have the same weight and also both the inner peaks have!) This means: The X-concentration of the reaction system (91) fluctuates mainly around either $x_{s,1}$ or $x_{s,4}$. Thus, contrary to the picture supported by the deterministic theory of the preceding section, because of its stochastics, the reaction system behaves as an "almost bistable system" also below its second non-equilibrium phase transition. Only in the special case of $\delta \ll \Delta$, the weights of the outer and the inner peaks become comparable to each other so that all four steady states (which now are metastable because of the stochastics) are statistically relevant.

In the $\delta \ll \Delta$-case, also a qualitative statement about the life-times of the metastable steady states can be made. If the reaction system starts, e.g., at the steady state $x_{s,1}$ (or $x_{s,2}$), i.e., if $\varrho(x;t)$ has initially only a single peak around $x_{s,1}$ (or $x_{s,2}$), this probability distribution then relaxes to a doubly peaked distribution with peaks around $x_{s,1}$ and $x_{s,2}$ on a time scale that is proportional to $\exp(\delta^4 V/D)$. Only on the much greater time scale $\exp(\Delta^4 V/D)$, $\varrho(x;t)$ finally approaches the stationary solution $\varrho_\infty(x)$ (with four peaks of approximately equal weight).

What are the consequences for the amount of information being stored? As was the case for the Schlögl model discussed in Chapt. III, also the model system considered here shows a quasi-conservation of just one "bit" in the region below its upper phase transition (if we neglect processes on a time scale larger than of order $\exp(\Delta^4 V/D)$!). Below the second transition, an additional amount of information becomes quasi-conserved. This additional amount approaches its maximum of one more "bit" in the $\delta \ll \Delta$-case, but the price to pay for its enlargement up to a full "bit" is that the time scale for its quasi-conservation becomes shortened, viz., $\exp(\delta^4 V/D)$.

VI.3. Increasing the Degree of Order by Increasing the Rates of Reactions of Higher Complexity

Contrary to the considerations in Chapts. III and V, here, the non-equilibrium phase transitions are imagined to be not induced by changing the *concentrations* of the initial and final reaction partners, a, b, and e, by control from outside, but rather by varying the reaction *parameters* k. In order to have some concrete values, we fix a, b, e, and x_0 by setting each of them equal to $1/5$ and assume the second bifurcation to take place when Δ reaches the value $\frac{1}{4}x_0$: We set $\delta^2 = \Delta^2 - (\frac{1}{4}x_0)^2$. In this special case, the values of the reaction parameters necessary for the reaction system (91) to show phase transitions as outlined in Sect. VI.1, are functions of Δ which remains the only independent variable. Expanding the k's up to terms quadratic in Δ and making the Δ-dependences resulting comparable to each other by dividing each of the k's by its value at $\Delta = 0$, we get

$$\frac{k_{\mu^{(\nu)}}(\Delta)}{k_{\mu^{(\nu)}}(0)} = \frac{g(\Delta)}{g(0)}\,(1 - c_{\mu^{(\nu)}}\,\Delta^2)\,; \qquad \nu = 1, 2, 3, 4; \quad \mu \triangleq \rightarrow, \leftarrow; \tag{94}$$

with

$$c^{(1)}_{\rightarrow} \cong 33.7, \quad c^{(1)}_{\leftarrow} \cong 20.7, \quad c^{(2)}_{\rightarrow} \cong 10.5, \quad c^{(2)}_{\leftarrow} \cong 3.6,$$
$$c^{(3)}_{\rightarrow} = 0, \quad c^{(3)}_{\leftarrow} = 0, \quad c^{(4)}_{\rightarrow} \cong 49.2, \quad c^{(4)}_{\leftarrow} \cong 66.7\,.$$

Since the reaction scheme (91) contains four classes of reaction steps, viz., tri-, penta-, heptamolecular reaction steps, and a usual synthesis-decay-reaction, we introduce the averages

$$\bar{k}^{(\nu)}(\Delta) = \tfrac{1}{2}\left(k^{(\nu)}_{\leftarrow}(\Delta)/k^{(\nu)}_{\leftarrow}(0) + k^{(\nu)}_{\rightarrow}(\Delta)/k^{(\nu)}_{\rightarrow}(0)\right),$$

$\nu = 1, 2, 3, 4$, as reaction parameters each characterizing one of these classes.

Now we use the picture that the reaction steps (91.4) serve as the basis of the reaction scheme (91) and that the multimolecular reactions enter into competition to (91.4) more and more when Δ increases. For this picture to apply, we assume $\bar{k}^{(4)}$ to be independent of Δ, $\bar{k}^{(4)}(\Delta) \equiv 1$, which in turn determines the function $g(\Delta)$ unknown till now, and we get

$$\bar{k}^{(\nu)} = 1 + c_\nu \Delta^2\,, \quad \nu = 1, 2, 3, \tag{95}$$

with

$$c_1 \cong 30.8, \quad c_2 \cong 50.9, \quad c_3 \cong 58.0\,.$$

As the result, we can state the following: If the *concentrations* of the initial and final substances are kept at constant values, the *reaction parameters* must be changed in order to bring the reaction system (91) through non-equilibrium phase transitions. The direction of the k-variations has to be such that the relative effectiveness of the multimolecular reactions (compared to that of the basic reaction steps (91.4)!) increases and, what is more that the rate of that increase of effectivity in turn must increase when going from the tri- over the penta- to the heptamolecular reactions. Therefore, the most highly multimolecular reaction steps become most important when bringing the system from its one-steady-state phase across the bistability regime into its four-steady-state phase.

Since multimolecular reaction steps are extremely rare in real chemical reaction systems, the reaction scheme (91) seems to be highly artificial. But to get contact to a more realistic background, we may imagine the multimolecular reaction steps each as a shortened form of a series of bimolecular reactions with catalytic and autocatalytic reaction steps, e.g.,

$$A + 2X \rightarrow 3X \Leftrightarrow A + X \rightarrow Y, \quad Y + X \rightarrow 3X\,.$$

This is in fact approximately possible if the concentrations of the intermediates dropped in the shorted form have much faster relaxation processes than the X-concentration so that the x-variable remains the leading variable ("the" order parameter!) within the differential equations describing the reaction kinetics of the full reaction system [4]. Then, in generalization of the model system (91), we can say: If a reaction system shows an evolution process in the sense that, in the course of time, selfproduced catalysers appear which enhance especially the effectiveness of reaction series corresponding to higher multimolecular reaction steps, or which enable more complex reaction steps than those already working, then the reaction system has the possibility to increase the complexity of its steady state constellation by going successively through non-equilibrium phase transitions and, by this, to also increase the information content.

Conclusions and Outlook

After this rather rough speculation about an evolving reaction system with only one order parameter, let us summarize the basic points of this paper.

We tried to find an information concept that includes static as well as dynamic aspects of chemical reaction systems. For that purpose, we defined two information measures, viz., $J(\alpha/\varrho_\infty)$ which denotes the average amount of information one gets by doing a measurement with an detector characterized by the parameter set α, and $J(\alpha/\varrho_\infty; t - t_*)$ which indicates the conservation of an arbitrary message having once been detected, within the reaction system. These quantities are based on the assumption that the stochastics of the reaction kinetics can be properly described by a Markovian process, which was introduced in Chapt. II by the so called "birth and death" master equation, and which we treated in the Fokker-Planck approximation. The time dependence of the probability distributions governed by that Markovian process was needed to predict theoretically the results the detector possibly will give us by a measurement, whereas the stationary probability distributions, ϱ_∞, which come out as the limiting distributions of the Markovian process, are used, on one hand, as reference distributions necessary in order to express the information gain we get by actually doing a detector measurement and, on the other hand, for averaging over all possible detector outputs. Correspondingly, the information measures contain parameters which characterize the dynamical behaviour of the concentration fluctuations (especially: characteristic relaxation times) and such parameters which represent the steady state behaviour. (Because of their peaked structures, the stationary distributions reflect the steady state constellation determined by the deterministic reaction kinetics of the reaction system!) But, what is the essential point, the information measures defined do not depend on any kind of initial conditions, i.e., the amount of all the information that has to do with a special initial preparation of the reaction system and which, for this reason, is not uniquely determined by the parameters of the reaction system itself, is excluded.

As pointed out in Chapts. III to VI, chemical reaction systems are able to store a certain amount of information if they exhibit at least one non-equilibrium phase transition and if they stay in a phase that is separated from the thermal equilibrium regime by such a transition. But in all the cases treated, this was only a quasi-conservation of information, i.e., a conservation during a large, but finite time interval. In order to obtain real information storage without any loss, one has to enlarge the volume of the reaction system to infinity, $V \rightarrow \infty$. (Note that the life-times of the metastable steady states go to infinity in this limit so that the steady states become really stable.) However, in the framework of the present paper, this limit is of no concrete meaning because, for $V \rightarrow \infty$, our assumption of a spatially homogeneous reaction system certainly breaks down. This shows the necessity to deal with stochastic reaction kinetics which take into account also the transport of the reaction partners within the reaction volume [48, 3, 4]. Correspondingly, also the information measures then must be generalized so that real space structures can be embraced into the information concept.

Another limitation of the present considerations is the following: We introduced the stochastics not by a projection from the real microscopic (many body) behaviour of the reaction systems, but rather we firstly treated the deterministic reaction kinetics which include as many variables as there are intermediates present (i.e., the many body problem is already reduced to a "few body" problem), and then we introduced stochastics by allowing these variables to fluctuate in the framework of a Markovian process. For an arbitrary reaction system capable of increasing its complexity by successively producing better and better catalysers and autocatalysers, one may presume that the projection from the real microscopics will in general not result in a stochastic process of the Markovian kind. Thus, it should be useful to generalize the information concept also to non-Markovian processes. The main difficulty in doing this, is that there no longer exists a stationary (limiting) probability distribution. A first attempt to overcome this problem will be given in a future communication.

Acknowledgements

I am indebted to Prof. Dr. M. Eigen for grant of a MPG-fellowship and for making possible a cooperation with Dr. P. H. Richter and Dr. F. Jähnig, to whom I am very grateful for several stimulating discussions and for their patience when I did my first steps within the area being the subject of this paper.

I wish to express my thanks to Prof. Dr. H. Hahn for suggesting this investigation, for arranging the cooperation with the MPI, for his continuous interest and encouragement during the work and for critically reading the manuscript.

[1] M. Eigen and R. Winkler, Das Spiel — Naturgesetze steuern den Zufall, Piper, München 1975.
[2] P. Glansdorff and I. Prigogine, Thermodynamic Theory of Structure, Stability and Fluctuations. Wiley-Interscience, New York 1971.
[3] G. Nicolis and I. Prigogine, Self-Organization in Nonequilibrium Systems, Wiley-Interscience, New York 1977.
[4] H. Haken, Synergetics — Nonequilibrium Phase Transitions and Self-Organization in Physics, Chemistry and Biology, Springer, Heidelberg 1977.
[5] W. Ebeling, Strukturbildung bei irreversiblen Prozessen, Teubner, Leipzig 1976.
[6] I. Prigogine and R. Lefever, Theory of Dissipative Structures, in: Synergetics, see [7].
[7] H. Haken (Ed.), Synergetics — Cooperative Phenomena in Multi-Component Systems, Teubner, Stuttgart 1973.
[8] E. Schrödinger, What is Life ?, Cambridge Univ. Press, London 1945.
[9] M. Eigen, Selforganization of Matter and the Evolution of Biological Macromolecules, Naturwiss. **58**, 465 (1971).
[10] H. Quastler, The Emergence of Biological Organization, Yale Univ. Press, New Haven, Conn. 1964.
[11] L. Brillouin, Science and Information Theory, Academic Press, New York 1956.
[12] E. v. Weizsäcker, Erstmaligkeit und Bestätigung als Komponenten der Pragmatischen Information, in: Offene Systeme I (E. v. Weizsäcker, ed.), Klett, Stuttgart 1974.
[13] M. V. Volkenstein, The Amount and Value of Information in Biology, Foundations of Phys. **7**, 97 (1977).
[14] P. H. Richter, Evolution — eine Folge von Phasenübergängen, Physik in unserer Zeit **56**, 43 (1974).
[15] A. Rényi, Wahrscheinlichkeitsrechnung, VEB, Deutscher Verlag der Wissenschaften, Berlin 1973.
[16] R. V. Hartley, Bell-Syst. Techn. J. **7**, 535 (1928).
[17] C. E. Shannon, Bell. Syst. Techn. J. **27**, 379 and 623 (1948). — C. E. Shannon and W. Weaver, The Mathematical Theory of Communication, Univ. Illinois Press, Urbana 1949.
[18] N. Wiener, Cybernetics or Control and Communication in the Animal and the Machine, Wiley, New York 1951.
[19] F. J. Zucker, Information, Entropie, Komplementarität und Zeit, in: Offene Systeme, see [12].
[20] S. Kullback, Ann. Math. Statist. **22**, 79 (1951); Information Theory and Stastistics, Dover, New York 1961.
[21] S. W. Benson, The Foundations of Chemical Kinetics, Mc Graw-Hill, New York 1960.
[22] D. A. McQuarry, Stochastic Approach to Chemical Kinetics, in: Suppl. Rev. Ser. Appl. Prob., Methuen, London 1967.
[23] F. Jähnig and P. H. Richter, J. Chem. Phys. **64**, 4645 (1976).
[24] A. T. Bharucha-Reid, Elements of the Theory of Markov Processes and Their Applications, McGraw-Hill, New York 1960.
[25] S. R. de Groot and P. Mazur, Non-Equilibrium Thermodynamics, North-Holland Publishing, Amsterdam 1962.
[26] K. Tomita and H. Tomita, Prog. Theor. Phys. **51**, 1731 (1974); K. Tomita, T. Ohta and H. Tomita, Prog. Theor. Phys. **52**, 1744 (1974).
[27] R. Görtz and D. F. Walls, Z. Phys. B **25**, 423 (1976). G. Haag, W. Weidlich, and P. Alber, Z. Phys. B **26**, 207 (1977).
[28] F. Schlögl, Z. Physik **191**, 81 (1966), **198**, 559 (1967), **243**, 303 (1971), **248**, 446 (1971); Stability Criteria in Non-Equilibrium Thermodynamics, in: Synergetics, see [7].
[29] E. Ruch and A. Mead, Theoret. Chim. Acta **41**, 95 (1976).
[30] R. Kubo, K. Matsuo, and K. Kitahara, J. Stat. Phys. **9**, 51 (1973).
[31] F. Schlögl, Z. Physik B **25**, 411 (1976).
[32] H. Haken, Rev. Mod. Phys. **47**, 67 (1975).
[33] N. G. vanKampen, Can. J. Phys. **39**, 551 (1961).
[34] H. Hasegawa, Prog. Theor. Phys. **57**, 1523 (1977).
[35] F. Schlögl, Z. Physik **253**, 147 (1972).
[36] H. E. Stanley, Introduction to Phase Transitions and Critical Phenomena, Clarendon Press, Oxford **1971**.

[37] H. K. Janssen, Z. Physik **270**, 67 (1974).
[38] T. Shimizu, Physica **91 A**, 534 (1978).
[39] Y. Saito, J. Phys. Soc. Japan **41**, 388 (1976).
[40] J. Schnakenberg, Thermodynamic Network Analysis of Biological Systems, Springer, Heidelberg 1977.
[41] I. Prigogine and R. Lefever, J. Chem. Phys. **48**, 1695 (1968).
[42] J. Tyson, J. Chem. Phys. **58**, 3919 (1973).
[43] J. Schnakenberg, preprint 1978.
[44] A. J. Lotka, Proc. Nat. Acad. Sci. (USA) **6**, 420 (1920); Elements of Mathematical Biology, Dover, New York 1956.
[45] V. Volterra, Leçons sur la Theorie Mathematique de la Lutte pour la Vie, Gauthier-Villars, Paris 1936.
[46] N. S. Goel, S. C. Maitra, and E. W. Montroll, Rev. Mod. Phys. **43**, 231 (1971).
[47] I. Decker and H. Hahn, Physica **93 A**, 215 (1978); to be published.
[48] C. W. Gardiner, K. J. McNeil, D. F. Walls, and I. S. Matheson, J. Stat. Phys. **14**, 309 (1976).
[49] N. G. vanKampen, J. Stat. Phys. **17**, 71 (1977).
[50] G. Nicolis and J. W. Turner, Physica **89 A**, 326 (1977).
[51] C. Escher, preprint 1979.
[52] Y. Kuramoto and T. Tsuzuki, Prog. Theor. Phys. **54**, 60 (1975).
[53] H. Mashiyama, A. Ito, and T. Ohta, Prog. Theor. Phys. **54**, 1050 (1975).
[54] J. Schnakenberg, preprint 1979.
[55] K. Matsuo, K. Lindenberg, and K. E. Shuler, J. Stat. Phys. **19**, 65 (1978).