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On Phase Transitions in Schlögl's Second Model

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We study Schlögl's second model, characterized by chemical reactions

$$2X \underset{k_2}{\overset{k_1}{\rightleftharpoons}} 3X, \quad X \underset{k_4}{\overset{k_3}{\rightleftharpoons}} 0,$$

in d-dimensional space. The reactions are assumed to be local; local fluctuations are fully taken into account, and particle transport occurs via diffusion.
In contrast to previous investigations, we find no phase transition when $k_4 \neq 0$ and $d<4$. For $k_4=0$, $k_3 \neq 0$, and $1 \leqq d<4$, we find a second-order phase transition which is in the same universality class as the transition in Schlögl's first model. Only for $d \geqq 4$ we do find the first-order transition found also by previous authors.
These claims are supported by extensive Monte Carlo calculations for various realizations of this process on discrete space-time lattices.

1. Introduction

Instabilities in systems far from equilibrium have been studied very intensively during the last years [1, 2]. The variety of phenomena observed there is extremely rich, reaching from close analogies of equilibrium phase transitions to such phenomena like self-generated chaos.
In this paper we shall study transitions between two stationary states in models for autocatalytic chemical reactions. Two such models were introduced by Schlögl [3], and studied later in great detail as prototype models with second order resp. first order transitions. They are characterized by the reactions

$$X \underset{\kappa_2}{\overset{\kappa_1}{\rightleftharpoons}} 2X, \; X \underset{k_4}{\overset{k_3}{\rightleftharpoons}} 0 \qquad \text{(model I)} \tag{1.1}$$

and by

$$2X \underset{k_2}{\overset{k_1}{\rightleftharpoons}} 3X, \; X \underset{k_4}{\overset{k_3}{\rightleftharpoons}} 0 \qquad \text{(model II)}. \tag{1.2}$$

The rate equations are

$$\frac{dn}{dt}=k_4-k_3 n+\kappa_1 n-\kappa_2 n^2 \qquad \text{(model I)} \tag{1.3}$$

and

$$\frac{dn}{dt}=k_4-k_3 n+k_1 n^2-k_2 n^3 \qquad \text{(model II)}. \tag{1.4}$$

By suitable rescalings, we can always put

$$\tfrac{1}{3}k_1=k_2=\kappa_1=\kappa_2=1. \tag{1.5}$$

Model I is in this approximation just the well-known Malthus-Verhulst population model. The stationary solution of (1.3) shows a bifurcation for $k_4=0$:

$$n=\begin{cases}0 & \text{for } k_3>1\\ 1-k_3 \text{ or } 0 & \text{for } k_3<1\end{cases} \tag{1.6}$$

(see Fig. 1a), resembling a second order phase transition. For $k_4>0$, there is no sharp transition.
The equation determining the stationary state of Model II,

$$k_4-k_3 n+3n^2-n^3=0, \tag{1.7}$$

has either one real and two complex solutions or three real solutions, depending on the rates k_3 and k_4 (see Fig. 1b). In the latter case, only two of these

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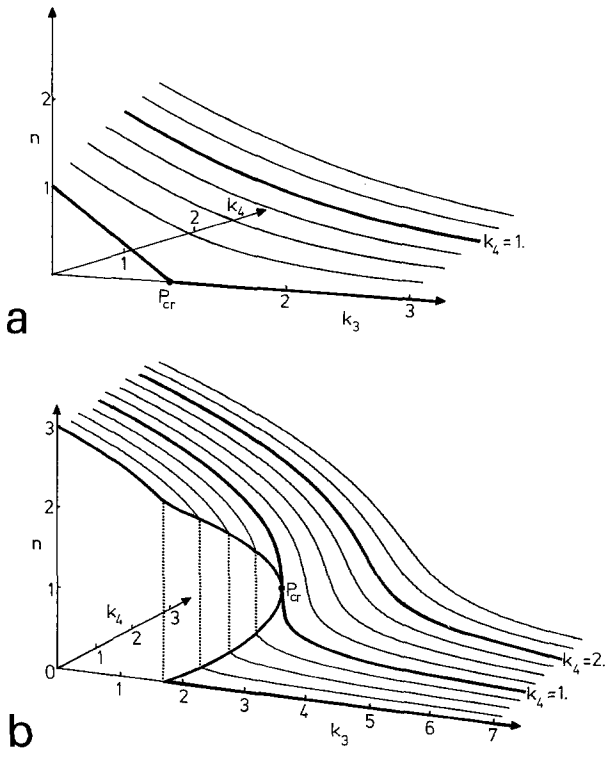

Fig. 1. Phase diagrams in the rate approximation. a) Model I, with $\kappa_1=\kappa_2=1$, b) Model II, with $k_1=3$, $k_2=1$

solutions are stable under small fluctuations, and the model shows a first order transition. For

$$k_4=k_2=1, \quad k_3=k_1=3, \quad n=1, \tag{1.8}$$

one has a triple solution corresponding to a critical point, i.e. a second order transition. All this becomes fairly obvious by noting the similarity of (1.7) with the van der Waals-equation [3].

Now we may ask how these results are modified by fluctuations, if we treat the models as Markov processes.

In the simplest case, one might assume the systems to be well stirred, so that the positions of the particles are irrelevant. In this case, the natural description is by a nonlinear death- and birth-model [4]. The results (1.6)-(1.8) are then recovered in the limit of large systems - where, however, the assumption of perfect stirring becomes unrealistic.

For a more realistic description, one should use a reaction-diffusion model, with local interactions and local fluctuations. This is what we shall do in the present paper.

If one assumes the interactions to be strictly point-like, one encounters the usual short-distance divergences [5, 6], hence one has to resort to some regularization prescription. Each different regularization defines of course a different model, but one expects all to have essentially the same phase structure, and in particular to have the same critical behaviour near a second order phase transition.

In this sense, model I is equivalent to a large number of models which have been studied independently in various fields of science: to reggeon field theory [7, 8], to directed percolation [9, 10], and to the basic contact model [11] which itself is isomorphic to the reggeon spin model [12, 13]. As a consequence, its critical behaviour is very well known [13-17].

The situation is different for model II. There exist several calculations [18-20] based on Langevin and multi-variate master equations, all of which claim to verify the results of the rate equation: they find (for $d\geqq 2$; $d=$number of dimensions) a first order transition, and a critical point (with $k_4\neq 0$) which is in the same universality class as the Ising model. If true, this would be a most remarkable extension of the universality hypothesis, from models with detailed balance to models without it.

There exists in addition a Monte Carlo simulation of model II, putting it on a lattice in space with continuous time [21]. For $d=1$, the authors do not find a phase transition. For $d=2$, their results are inconclusive, although suggestive of a transition in agreement with [18-20].

In contrast to this, we shall present formal arguments and rather detailed Monte Carlo calculations which show clearly that there is *no sharp transition* for $d<4$, and for $k_4\neq 0$. We furthermore propose that for $k_4=0$ and $k_3\neq 0$ there is a second-order phase transition, which for $d<4$ is in the same universality class as the transition in model I. For $d=1,2$ and 3, the existence of this transition is clearly seen in the Monte Carlo calculations, but only for $d=1$ our data are sufficient to indicate that it has indeed the same critical behaviour as model I. For $d\geqq 4$, the transition at $k_4=0$ becomes of first order.

Our Monte Carlo simulations relied on the universality hypothesis. Using this hypothesis, we simplified the model drastically, as compared e.g. to that of [21]. First, we discretized time in addition to space. Secondly, we substituted the saturation reaction $3X\to 2X$ by assuming that any lattice point can be at most doubly occupied. Finally, some other modifications will be described later in detail. In order to test the universality hypothesis we also studied several other versions. They all showed qualitatively similar behaviour.

When making such modifications, one has of course to take care not to destroy the essential properties of the model. These properties of model II, as compared to model I, are (1) that saturation effects set in

only when $\geqq 3$ particles meet, and (2) that autocatalytic production occurs only when $\geqq 2$ particles meet. They are satisfied in all our versions. We also checked that the mean-field approximations to our modified models (valid in the limit $d \to \infty$) show first order transitions which are in surprisingly good agreement with our Monte Carlo results for $d=4$.
In the next section, we present the general formalism and the standard argument leading to an Ising-type behaviour of Model II. Conflicting formal and heuristic arguments are given in Sect. 3. In Sect. 4, we shall define the lattice model for which the most detailed Monte Carlo calculations have been performed, and present their results. Finally, in Sect. 5 we end with a comparison of our approach with the approach of [21], and with some concluding remarks.

2. Formal Developments

a. Operator Formulation

We shall use here the Fock-space methods developed in [6] and [22], employing essentially the notation of [6]. There, annihilation and creation fields $\psi(\mathbf{x})$ and $\pi(\mathbf{x})$ with the usual commutation relations and with $\psi|0\rangle=0$ were introduced. The time evolution of a state $|\Phi(t)\rangle$ is described by

$$\frac{\partial}{\partial t}|\Phi(t)\rangle = L|\Phi(t)\rangle, \tag{2.1}$$

with the Liouville operator L depending on the specific model considered. Defining a scalar product such that

$$\pi(\mathbf{x}) = 1 + \xi^2 \psi^+(\mathbf{x}) \tag{2.2}$$

with ξ being an arbitrary positive constant of dimension $l^{d/2}$, the n-particle densities (correlation functions) in a state Φ at time t are

$$\rho_n(\mathbf{x}_1, \ldots \mathbf{x}_n, t) = \langle 0|\psi(\mathbf{x}_1) \ldots \psi(\mathbf{x}_n)|\Phi(t)\rangle. \tag{2.3}$$

If all reactions are strictly local, the two Schlögl models are defined by Liouvillean densities ($L = \int d^d x\, \mathscr{L}(x)$)

$$\mathscr{L}_\mathrm{I} = -D\nabla\pi\cdot\nabla\psi + \kappa_1(\pi^2-\pi)\psi + \kappa_2(\pi-\pi^2)\psi^2 + k_3(1-\pi)\psi + k_4(\pi-1) \tag{2.4}$$

and

$$\mathscr{L}_\mathrm{II} = -D\nabla\pi\cdot\nabla\psi + k_1(\pi^3-\pi^2)\psi^2 + k_2(\pi^2-\pi^3)\psi^3 + k_3(1-\pi)\psi + k_4(\pi-1), \tag{2.5}$$

with D being the diffusion coefficient. For model I, this was shown in [6]; for model II, it is easily found by applying the rules given there.
In view of (2.2) we put

$$\psi(\mathbf{x}) = \xi^{-1}\varphi(\mathbf{x}), \quad \pi(\mathbf{x}) = 1 + \xi\varphi^+(\mathbf{x}), \tag{2.6}$$

and get

$$\mathscr{L}_\mathrm{I} = -D\nabla\varphi^+\cdot\nabla\varphi + (\kappa_1-k_3)\varphi^+\varphi + \xi\kappa_1\varphi^{+2}\varphi - \frac{\kappa_2}{\xi}\varphi^+\varphi^2 - \kappa_2\varphi^{+2}\varphi^2 + k_4\xi\varphi^+ \tag{2.7}$$

and

$$\mathscr{L}_\mathrm{II} = -D\nabla\varphi^+\cdot\nabla\varphi - k_3\varphi^+\varphi + \frac{k_1}{\xi}\varphi^+\varphi^2 + k_1\varphi^{+2}(2+\xi\varphi^+)\varphi^2 - \frac{k_2}{\xi^2}\varphi^+(1+\xi\varphi^+)^2\varphi^3 + k_4\xi\varphi^+. \tag{2.8}$$

The advantage of this transformation is that

$$\langle 0|\varphi^+(\mathbf{x}) = 0 \tag{2.9}$$

while $\langle 0|\pi(\mathbf{x}) = \langle 0|$.
One sees immediately from (2.7) and (2.8) that model I is renormalizable for $d<3$ while model II is non-renormalizable, if expanded about the vacuum state, for all $d \geqq 2$.
We might add that the fields $\hat{\pi}$ and $\hat{n}$ of [19] are closely related to our fields:

$$\hat{\pi}(\mathbf{x}) = i\ln\pi(\mathbf{x}), \quad \hat{n}(\mathbf{x}) = \pi(\mathbf{x})\psi(\mathbf{x}). \tag{2.10}$$

With this transformation, the "hamiltonian" of [19] is easily seen to coincide with our $\mathscr{L}_\mathrm{II}$.

b. Critical Behaviour of Model I

For $k_4=0$ the critical behaviour of model I has been studied among others by the $\varepsilon=4-d$-expansion [14], by a high-"temperature" expansion [15], and by Monte Carlo methods [13]. We shall quote here only some results which later will prove useful for understanding model II.
Let us first note that $\mathscr{L}$ has dimensionality $t^{-1}l^{-d}$, while

$$[\varphi] = [\varphi^+] = l^{-d/2}. \tag{2.11}$$

From this one sees the quartic term $\kappa_2\varphi^{+2}\varphi^2$ is irrelevant near the phase transition. Dropping this term does not change the critical behaviour. If we would drop, in contrast, all "irrelevant" terms in $\mathscr{L}_\mathrm{II}$, we would end up with a trivial theory.

As shown in [14], the existence of a renormalization group fixed point depends crucially on the anti-hermiticity of the cubic couplings, i.e. on the opposite signs of the terms $\varphi^+\varphi^2$ and $\varphi^{+2}\varphi$. Another necessary condition is $\kappa_1 > k_3$.
The upper critical dimension is $d_+ = 4$, the lower is [13, 15] $d_- = 1$. In qualitative agreement with the rate approximation, there exists a critical value of k_3 (for κ_1 and κ_2 fixed, $k_4 = 0$) such that there are two stationary states for $k_3 < k_{3,cr}$: the vacuum and a state with

$$n \equiv \rho_1(\mathbf{x}) \approx \rho_0 (k_{3,cr} - k_3)^\beta, \quad \beta > 0. \tag{2.12}$$

For $k_3 = k_{3,cr}$, all configurations with finitely many particles die out: the chance P_t to find at least one particle at time $t \gg 0$ in a state which had started with a finite number of particles at $t = 0$ decreases as

$$P_t \underset{t\to\infty}{\approx} p_0 t^{-\delta}, \quad \delta > 0, \tag{2.13}$$

although the average particle number increases as

$$\langle n \rangle_t \approx n_0 t^\eta, \quad \eta > 0. \tag{2.14}$$

The exponents β, δ, and η (and other critical exponents) can be found e.g. in [10, 13, 15-17].
The strong clustering expressed in (2.12) and (2.13) is also seen by looking at $\rho_2(\mathbf{x}, \mathbf{y}, t)/\rho_1(\mathbf{x}, t)$. This is the conditional probability density to find a particle near $\mathbf{y}$, provided there is at the same time a particle at $\mathbf{x}$. For large times, one finds for $k_3 \approx k_{3,cr}$ and finite $|\mathbf{x} - \mathbf{y}|$

$$\frac{\rho_2(\mathbf{x}, \mathbf{y}, t)}{\rho_1(\mathbf{x}, t)} \approx \frac{c}{|\mathbf{x} - \mathbf{y}|^\gamma}, \quad \gamma = \frac{d\delta}{2\delta + \eta}. \tag{2.15}$$

Thus, the chance to find a second particle at a finite distance from any given particle does not go to zero at the critical point, in contrast to the assumption underlying the rate approximation.
At $d = 4$, clustering may still be strong, but it no longer dominates the critical behaviour: the exponents ($\delta = 1$, $\eta = 0$, and $\beta = 1$) are precisely those obtained from the rate approximation. This expresses just the fact that the chance for any two particles to meet is essentially independent, for $d \geqq 4$, of their origin (whether they come from the same "ancestor" or not), and thus clusters can not evolve as coherent objects.

c. Critical Behaviour of Model II

According to the rate approximation and to [18-21], we should expect a critical point for $k_4 > 0$, with a stationary density $n \neq 0$. This suggests replacing φ by a shifted field χ, with

$$\chi(\mathbf{x}) = \varphi(\mathbf{x}) - n\xi, \tag{2.16}$$

so that

$$\langle 0 | \chi(\mathbf{x}) | \Phi_{\text{stat}} \rangle \approx 0. \tag{2.17}$$

The conjugate field φ^+ should not be shifted.
Under this shift, $\mathscr{L}_{\text{II}}$ is transformed into

$$\mathscr{L}_{\text{II}} = \varphi^+ F(\chi) - \varphi^{+2} Q + \tilde{\mathscr{L}}_{\text{II}} \tag{2.18}$$

with

$$F(\chi) = D\nabla^2 \chi + \xi(k_4 - k_3 n + k_1 n^2 - k_2 n^3) + (2k_1 n - k_3 - 3k_2 n^2)\chi + \frac{1}{\xi}(k_1 - 3k_2 n)\chi^2 - \frac{1}{\xi^2} k_2 \chi^3, \tag{2.19}$$

$$Q = (3k_2 n - k_1)\xi^2 n^2, \tag{2.20}$$

and $\tilde{\mathscr{L}}_{\text{II}}$ containing all higher terms.
One finds that all terms lumped into $\tilde{\mathscr{L}}_{\text{II}}$ are irrelevant under the renormalization group [19]. This is most easily seen by making the further transformation

$$\varphi^+ \to \xi^{2/d} \bar{\varphi}^+, \quad \chi \to \xi^{-2/d} \bar{\chi}, \tag{2.21}$$

such that $[\bar{\varphi}^+] = l^{-1-d/2}$ and $[\bar{\chi}] = l^{1-d/2}$. Then all coupling constants in $\tilde{\mathscr{L}}_{\text{II}}$ have positive dimension of length [19], for $d \approx 4$.
Neglecting $\tilde{\mathscr{L}}_{\text{II}}$, one gets however a theory with detailed balance. The equation $\int d^d x \, \mathscr{L}_{\text{II}} |\Phi\rangle = 0$ for the stationary state is thus equivalent to

$$\{F(\chi) - \varphi^+ Q\} |\Phi\rangle = 0, \tag{2.22}$$

with the solution

$$|\Phi\rangle = \int [d\alpha] \, e^{\int d^d x \left\{\alpha(\mathbf{x})\varphi^+(\mathbf{x}) + \frac{1}{Q}\mathscr{F}(\alpha(\mathbf{x}))\right\}} |0\rangle, \tag{2.23}$$

$$\mathscr{F}(X) = \int_0^X d\chi \, F(\chi). \tag{2.24}$$

This state is easily seen to be just the equilibrium state of φ^4-theory with $kT = Q$ and $\mathscr{H} = -\mathscr{F}$.
Thus the critical behaviour of model II is, according to this standard treatment, exactly that of the Ising model.

3. Arguments Against the Standard Treatment of Model II

a. $d = 1$

The first argument against the conclusion that model II has an Ising-type critical point comes from considering $d = 1$.

For $d=1$, model I is well known to show a critical point (at $k_4=0$) [11, 13, 15, 16]. At first sight, this seems to contradict the Mermin-Wagner theorem. This theorem is, however, not applicable as the stationary state of Model I is not a thermal equilibrium with a short-range hamiltonian.

In contrast, for model II the above treatment would suggest that there is indeed no phase transition for $d=1$. This difference between models I and II would be very hard to understand:

For $\kappa_3<\kappa_{3,cr}$, the stationary state of model I has a non-zero particle density n and a finite range ξ of correlations. Let us assume that in model II the interaction range is $\gtrsim\xi$, and that $k_1\approx\frac{1}{n}\kappa_1$ and $k_2\approx\frac{1}{n}\kappa_2$. Then it is easy to see that both models should have essentially the same stationary state. Since, on the other hand, $n\equiv 0$ for sufficiently large k_3, there must exist a singular point also for model II, with $k_4=0$.

b. $d>1$

For all $d<4$, very similar heuristic arguments suggest that the critical behaviour of models I and II is indeed the same - implying, of course, that the critical point of model II is also at $k_4=0$.

The essential difference between the two models is that in model II a *single* particle cannot produce offspring. Near the critical point, however, the ability of a single model-I-particle to produce such offspring becomes irrelevant: due to the strong clustering mentioned in the last section, there will always be a second particle near-by (on a length scale defined by the correlation length). The same is true of the reaction $2X\to X$, which near the critical point is indistinguishable from $3X\to 2X$.

Of course, this is only true for $d<4$. For $d\geqq 4$, clustering no longer dominates the critical behaviour of model I, and the two models are no longer equivalent. This implies that the constants ρ_0, p_0, n_0, and c in (2.12)-(2.15) must diverge for $d\nearrow 4$. We expect

$$\begin{matrix}\rho_0\to\infty\\ p_0, n_0,\ c\to 0\end{matrix}\quad\text{for } d\nearrow 4. \tag{3.1}$$

c. *Alternative Field Theoretic Treatment*

As we have already stressed, a perturbative treatment of $\mathscr{L}_{\mathrm{II}}$ about the vacuum is impossible: dropping in (2.8) all non-renormalizable terms, we end up with a trivial theory. The above arguments might explain this qualitatively: near the critical point, the basic entities are not single particles but clusters of particles.

This suggests that we make a transformation to new creation and annihilation operators which create resp. annihilate just such clusters. Let us assume that we are working on a hypercubic lattice in space, so that

$$[\psi(\mathbf{i}),\pi(\mathbf{j})]=\delta_{\mathbf{i},\mathbf{j}}. \tag{3.2}$$

Then one such transformation is*

$$\tilde{\pi}(\mathbf{i})=e^{a(\pi(\mathbf{i})-1)}=1+a\xi\,\tilde{\varphi}^+(\mathbf{i}), \tag{3.3}$$

$$\tilde{\psi}(\mathbf{i})=\frac{1}{a}\tilde{\pi}^{-1}(\mathbf{i})\,\psi(\mathbf{i})=(a\xi)^{-1}\,\tilde{\varphi}(\mathbf{i}). \tag{3.4}$$

One easily checks that $[\tilde{\psi}(\mathbf{i}),\tilde{\pi}(\mathbf{j})]=[\tilde{\varphi}(\mathbf{i}),\tilde{\varphi}^+(\mathbf{j})]=\delta_{\mathbf{i},\mathbf{j}}$, and that $\tilde{\varphi}|0\rangle=0$.

For $k_4=0$, the Liouvillean expressed in terms of the new variables $\tilde{\varphi}$ and $\tilde{\varphi}^+$ is

$$\begin{aligned}\mathscr{L}_{\mathrm{II}}=&-D\nabla\tilde{\varphi}^+\cdot\nabla\tilde{\varphi}+(ak_1-a^2k_2-k_3)\,\tilde{\varphi}^+\tilde{\varphi}\\&-(3ak_2-k_1)\,\xi^{-1}\tilde{\varphi}^+\tilde{\varphi}^2+\frac{a\xi}{2}[2(k_1-ak_2)\\&+\tfrac{1}{2}(ak_1-a^2k_2-k_3)]\,\tilde{\varphi}^+\tilde{\varphi}^2+\tilde{\tilde{\mathscr{L}}}_{\mathrm{II}}.\end{aligned} \tag{3.5}$$

Here, $\tilde{\tilde{\mathscr{L}}}_{\mathrm{II}}$ contains terms with higher derivatives (from the lattice approximation to $\nabla\pi\cdot\nabla\psi$) and/or higher powers of the fields. Assuming the constant a to be dimensionless, one has $[\tilde{\varphi}]=[\tilde{\varphi}^+]=l^{-d/2}$, and all terms of $\tilde{\tilde{\mathscr{L}}}_{\mathrm{II}}$ are irrelevant as compared to the terms written explicitly in (3.5). These latter terms are however just those of model I, suggesting that both models have indeed the same critical behaviour.

This argument is of course far from being rigorous. It does not say anything, in particular, about what happens at $d=4$. Also, the constant a has to be chosen appropriately in order to get the correct signs of the $\varphi^+\varphi^2$ and $\varphi^{+2}\varphi$ couplings. But it does not seem worse than the standard argument presented in the last section. The crucial assumption in both was that perturbatively irrelevant terms can be simply thrown away. While this should work in cases where the true solution is already close to the perturbative (i.e. deterministic) one, it can completely fail if this is not true.

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* In writing the right-hand side of (3.3), we have also changed the definition of the scalar product (and whence of hermitian conjugation). One is free to do this in the present formalism [6], and only with the new scalar product the analogon of (2.3) holds for the densities of clusters

d. Detailed Balance and the Interface between the Two Phases

The crucial property missed by the standard argument seems to be the lack of detailed balance in model II and, related to it, the existence of an absorbing state (the vacuum) if $k_4=0$. (The terms in $\mathscr{L}_{II}$ violating detailed balance are all "irrelevant".)
That the lack of detailed balance leads to problems in locating the transition of model II is well known. Assume that the k_i are such that the rate equation (1.4) has two stable solutions. Two different arguments have been proposed in order to decide which one is the abolutely stable state.
The first was proposed by Schlögl [3]. He adds a diffusion term to (1.4) and looks at the kink solutions interpolating between the stationary solutions. In general this kink will move, so that one of the solutions "eats up" the other. Equilibrium is thus defined by $v_{\text{kink}}=0$.
The other argument, proposed by Nicolis and others [23], assumes strict homogeneity, but includes (in contrast to the above) homogeneous fluctuations. In the bistable region, the master equation for finite volume has then a solution with two bumps. In the limit of infinite volume, one of the bumps becomes a δ-function, $P(n)\sim\delta(n-n_{\text{rate eq.}})$, while the other dies out, except exactly on the transition point $k_3=k_{3,\text{Nicolis}}$.
The problem is that, for fixed k_1, k_2 and $k_4<k_{4,cr}$, the predicted transition point $k_{3,\text{Schlögl}}$ is always larger than the transition point $k_{3,\text{Nicolis}}$ (see Fig. 2). For systems with (small) inhomogeneities *and* fluctuations, and with $k_{3,\text{Nicolis}}<k_3<k_{3,\text{Schlögl}}$, the following happens: assume that, at a particular instant, $n\approx n_>$ in the whole system. A roughly homogeneous fluctuation will sooner or later lead to a collapse leading to $n\approx n_<$ in some finite region. The kink at the boundary of this region will, however, move inwards, and after some time the original status will be restored. This permanent cycling is of course a manifestation of a lack of detailed balance, and it will wipe out the sharp transition, for $k_4\neq 0$.
This is seen more clearly by looking at the interface between the two phases, when $k_4=0$. In this case $k_{3,\text{Nicolis}}=0$, since any finite population will finally die for all $k_3>0$. Schlögl's construction leads, on the other hand, to $k_{3,\text{Schlögl}}=2$.
Let us now consider a "hyperstrip"

$$0\leqq x_1\leqq L,\qquad -\infty<x_i<\infty,\qquad i=2,\ldots,d.$$

At $x_1=L$, we take absorbing boundary conditions ($n=0$), while at $x_1=0$ we assume that particles are permanently fed in, leading to a non-zero density. Between these two surfaces, there must be an interface. According to the standard treatment, the transition is first order (we still assume $k_4=0$), and thus the width of the interface remains finite for $k_3\to k_{3,cr}$ (except when $k_3=k_{3,cr}$ *exactly*) and $L\to\infty$.
In order to see that this cannot be correct, assume $k_3=k_{3,cr}+\varepsilon$, with $\varepsilon>0$. Then the interface will be near $x_1\approx 0$. Its deterministic velocity would be positive, however, for sufficiently small ε. Thus the actual interface will be strongly influenced by fluctuations: there is a permanent sparkling off of clusters, all of which die sooner or later, due to fluctuations in size. Since, for $\varepsilon\to 0$, sufficiently large clusters can live arbitrarily long and move arbitrarily far, the interface will become increasily fuzzy in this limit.
This argument breaks down for $d\geqq 4$ where, as we have seen in the last section, a cluster no longer evolves as a coherent object.
A similar (albeit less drastic) effect is indeed seen when treating the model in the mean field approximation of [24]. There, one divides the system into cells, in each of which the particles react according to a master equation. Diffusion between cells is taken into account by adding to the reaction rate for $X\to 0$ a term proportional to D, and adding to the rate for $0\to X$ a term proportional to $\langle n\rangle D$. One finds that, for any $D>0$, the critical point is shifted towards a smaller value of k_4, as compared to the rate equation. We claim that, in a more exact treatment, it would be shifted to $k_4=0$.

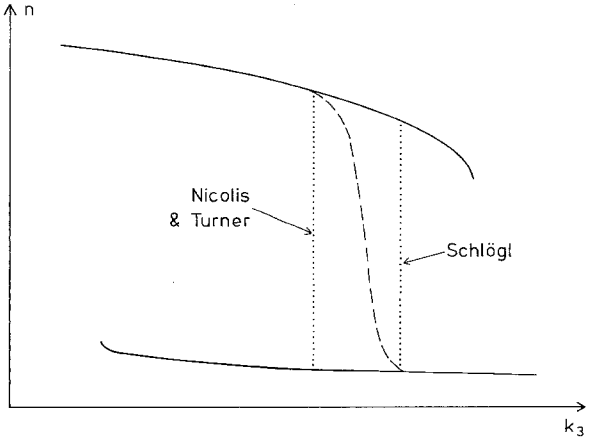

Fig. 2. Solid line: rate approximation for model II, with $k_4<k_{4,cr}$; dotted: transitions according to Schlögl [3] and Nicolis [23]; dashed: more realistic behaviour (schematic)

4. Monte Carlo Calculations

The arguments of the previous section can hardly be claimed to be rigorous. Thus, we dediced to support them by Monte Carlo calculations.

a. The Model

In order to obtain sufficient statistics, one can of course not perform molecular dynamics calculations with realistic interactions (e.g. hard spheres or Lennard-Jones potentials). Since we are interested only in the critical behaviour, this is also not necessary. Thus, we studied highly simplified models where we kept only those features which we considered essential.

In all models, we discretized both space and time, i.e. we replaced the space-time continuum by a $d+1$-dimensional cubic lattice. We also replace the saturation reaction $3X \to 2X$ by the prescription that any lattice point can be at most doubly occupied. The other reactions were simulated in a variety of different ways. A more or less random study of various models showed that all of them had the same qualitative behaviour. Some seemed however to have somewhat longer relaxation times than others, and some had transitions for very small values of k_3.

Finally, we settled down at the following model: each iteration $t \to t+1$ consists of four steps *(i)* to *(iv)*. During each step, the whole lattice is scanned through, and a set of new occupation numbers $\{m_\mathbf{i} = 0, 1, \text{ or } 2;\ \mathbf{i} = \text{site}\}$ are calculated from the previous set of occupation numbers $\{n_\mathbf{i}\}$. After the whole lattice has been scanned, the $n_\mathbf{i}$'s are replaced by the $m_\mathbf{i}$'s, and we go on to the next step. The four steps are:

(i) If site $\mathbf{i}$ is empty, we go to the next site. Otherwise, we choose a random number $0 < r_\mathbf{i} < 1$. If $r_\mathbf{i} < k_3$, and if site $\mathbf{i}$ is singly occupied, we remove the particle. If it is doubly occupied, we remove both particles if $r_\mathbf{i} < k_3^2$, and one if $k_3^2 < r_\mathbf{i} < 2k_3(1-k_3)$. This simulates the reaction $X \xrightarrow{k_3} 0$.

(ii) Similarly, we add a particle at site $\mathbf{i}$ with probability k_4, provided it is not already doubly occupied.

(iii) With probability 0.6 we go to the next site. Otherwise, and if site $\mathbf{i}$ is singly occupied, we move this particle with equal probability to one of its next neighbours. If $\mathbf{i}$ is doubly occupied, we move the two particles to opposite next neighbours. If this yields $\geqq 3$ particles in one of the neighbouring points, the surplus particle(s) is (are) simply discarded.

(iv) If and only if point $\mathbf{i}$ is doubly occupied, we add a particle in each of two neighbouring points $\mathbf{i} + \hat{e}_k$, and in the two opposite points $\mathbf{i} - \hat{e}_k$. For $d > 2$, the unit vectors $\hat{e}_k$ are chosen randomly. This simulates a reaction $2X \xrightarrow{k_1 = 1} 6X$, which in the rate approximation has the same effect as $2X \xrightarrow{k_1 = 4} 3X$. Again we discard any particle which is to be added to a site which is already doubly occupied.

b. Stationary States

The most extensive runs were performed in 2 dimensions. For given values of k_3 and k_4, we performed up to 9,600 iterations on lattice sizes up to 60×60, just ot obtain a stationary state. The same number of iterations then was used to calculate the average density n of particles per site, by calculating its mean value after every tenth iteration. In order to be sure that no hysteresis has remained, we performed sweeps with fixed k_4, and with k_3 both increasing and decreasing (except for $k_4 = 0$, where we made only one sweep with k_3 increasing). We started these sweeps with all sites doubly occupied. Helical boundary conditions were used, i.e. for a $N \times N$-lattice we identified $(i, N+1)$ with $(i+1, 1)$, and $(N, N+1)$ with $(1, 1)$.

A first search, the result of which is shown in Fig. 3a, showed the expected behaviour, intermediate between Figs. 1a and 1b. There is no sign of any singularity for $k_4 \neq 0$, but there is clearly a transition near $k_4 \approx 0$, $k_3 \approx 0.4$.

The results of detailed runs in the latter region are shown in Fig. 3b. We see that there is definitely no phase transition for $k_4 \gtrsim 0.01$, but there is a transition at

$$k_4 = 0, \quad k_3 = 0.3805 \pm 0.0005. \tag{4.1}$$

The data are not precise enough to decide whether it is indeed of second order (but they are compatible with it). This should not be surprising, as it should be of first-order in the absence of fluctuations.

There are three possible criticisms against our interpretation. First, one might suspect that the critical point is actually at a very small but non-zero value of k_4. Secondly, it might be that it is in the universality class of model I for *all* d, for some trivial reason. Third, our lattices might have been too small, so that the smoothness of the transition reflects only the finite lattice sizes. In order to eliminate these possibilities, we compare in Fig. 4 the results for $k_4 = 0.03$ with the results in 3 and 4 dimensions, also for $k_4 = 0.03$. As expected, the transition becomes steeper with increasing d. The 4-dimensional calculations strongly suggest a first-order transition, implying that the critical point has $k_4 > 0.03$. We notice that the 3- and 4-dimensional results were obtained on lattices of only 9^3 and 5^4 points, while the 2-dimensional results were obtained from 45×45 points. The iteration times were comparable in all 3 cases.

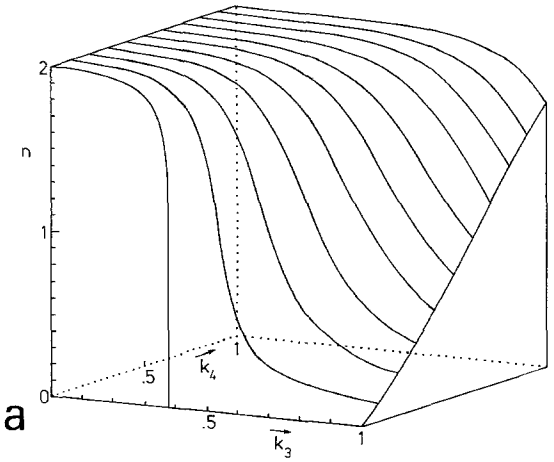

Fig. 3a. Monte Carlo phase diagram (density n of particles per site) for $d=2$. The continuous lines are curves $k_4=$const, hand-drawn through points whose errors where roughly of the same size as the thickness of the curves

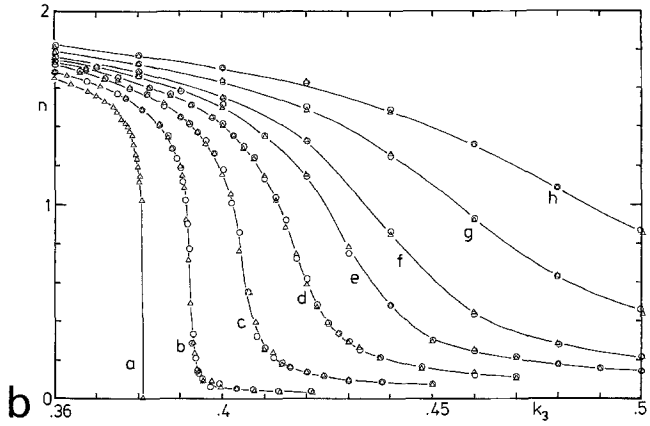

Fig. 3b. Average density n of sites per site near the phase transition for $d=2$. ○: sweeps with increasing k_3, with fixed k_4, △: sweeps with decreasing k_3, with fixed k_4. The continuous lines are only drawn for guidance. Curves: (a) $k_4=0$; (b) $k_4=0.01$; (c) $k_4=0.02$; (d) $k_4=0.03$; (e) $k_4=0.04$; (f) $k_4=0.05$; (g) $k_4=0.07$; (h) $k_4=0.1$

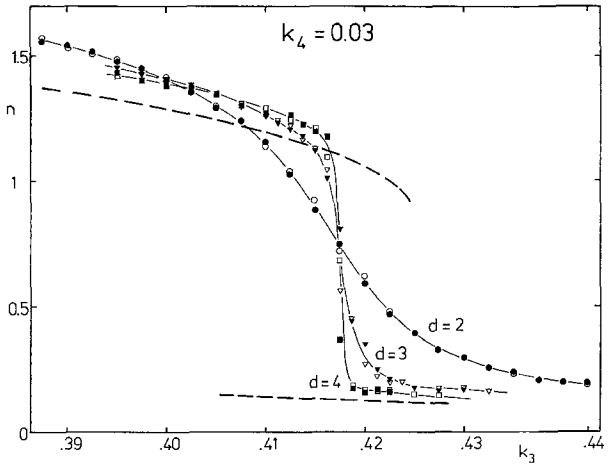

Fig. 4. Average density n for $k_4=0.03$ and $d=2$ (circles), 3 (triangles), and 4 (squares). Full symbols: sweeps with k_3 increasing. Open symbols: sweeps with k_3 decreasing. The dashed line is the result of the mean-field approximation

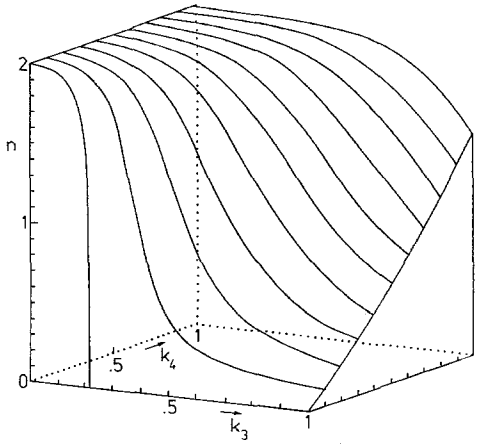

Fig. 5. Same as Fig. 2, but for $d=1$

Also shown in Fig. 4 is the result of the mean-field-approximation for our model. It is defined by replacing in steps *(iii)* and *(iv)* "neighbouring point" by "random point". It describes exactly the behaviour at $d\to\infty$. It leads to a critical point at $k_4\approx 0.05$. The location of the transition for $k_4=0.03$ cannot be determined without further assumptions (compare Sect. 3d).

As another check against a finite-size effect, we performed 2-dimensional calculations for $k_4=0.015$ on lattices 60×60 and 25×25. Within statistical errors, both showed exactly the same smooth transition.

Finally, we performed also calculations on one-dimensional lattices. If the critical behaviour were Ising-like as claimed in [18–20], we would not expect any transition. If it is the same as in model I, there should be a transition with qualitatively the same behaviour as in higher dimensions. For $d=1$, we have of course to modify step *(iv)*. We chose instead

Step *(iv')*: if point i is doubly occupied, we add one particle in $i+1$ and one in $i-1$, provided these points are not already doubly occupied.

The results, shown in Fig. 5, clearly show the expected transition at $k_4=0$ and $k_3=0.214\pm 0.001$. Although the transition is less steep than for $d=2$ (as we should have expected), it seems still hard to extract critical exponents from these data.

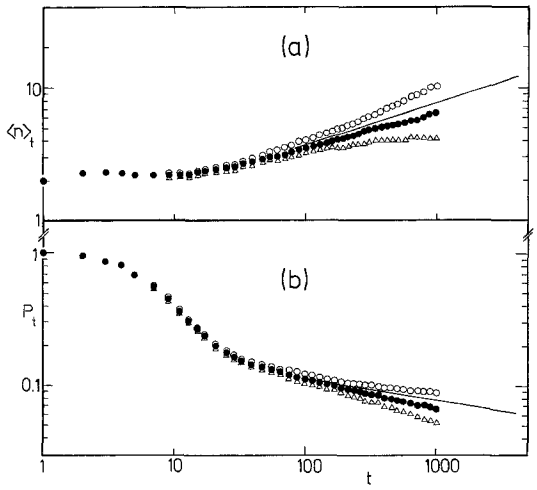

Fig. 6. Monte Carlo results for $\langle n \rangle_t$ (Fig. 5a) and P_t (Fig. 5b), for $d=1$. ○: $k_3=0.213$; ●: $k_3=0.215$; △: $k_3=0.217$. Data are based on 10^4 runs for each value of k_3. The straight lines have the slopes predicted by Eqs. (2.12) and (2.13)

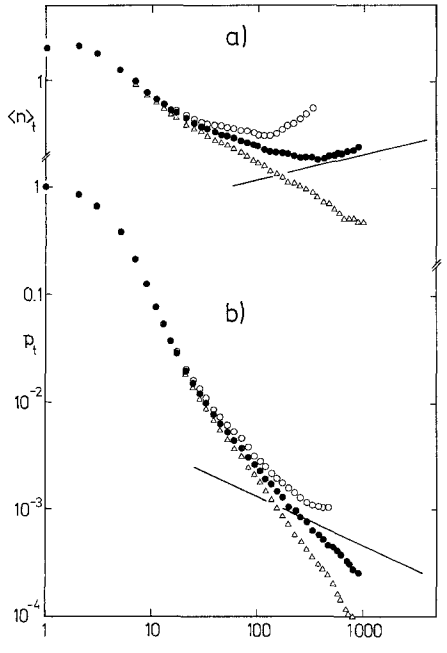

Fig. 7. Same as Fig. 6, but for $d=2$. ○: $k=0.378$ (5×10^4 runs, lattice 25×25); ●: $k=0.380$ (2×10^5 runs, lattice 35×35); △: $k=0.381$ (4×10^5 runs, lattice 33×33). Helical boundary conditions have been used. Due to the finite size of the lattices, there is a small systematic error shifting the very large-t data points to lower values. No corrections for this have been applied

c. Time-Dependent States

According to our experience with model I [13], it was easier to obtain rough values for these exponents from time-dependent states, by using (2.12) and (2.13). We thus performed also such calculations, for $k_4=0$, by starting with one doubly occupied site with all other sites empty, and watching the evolution for typically $\sim$1,000 iterations.

Such calculations are particularly effective for $d=1$, where we can choose the lattice large enough so that no particle ever reaches its boundary. There, we can also easily restrict the iterations to that part of the lattice which is not empty.

The results of $\langle n \rangle_t$ are shown in Figs. 6a ($d=1$) and 7a ($d=2$), those for P_t in Figs. 6b and 7b. For comparison, also the predictions from (2.13) and (2.14) are shown. For $d=1$, as expected, scaling sets in later than in the model I calculations in [13]. Nevertheless, the data seem to agree with the predictions. For $d=2$, scaling sets in even later. Again this was expected - for $d=4$, we do not expect any scaling behaviour at all -, but it makes any comparison with the predictions meaningless.

5. Discussion

The Monte Carlo simulations of the last section clearly show that there is no first-order transition in Schlögl's second model. They also indicate (although less clearly) that the observed second-order transition is in the same universality class as the one in Schlögl's first model. Both conclusions are in agreement with our prediction based on formal and heuristic arguments, but in striking disagreement with [18-20].

The Monte Carlo calculations of Hanusse et al. [21] indicated no phase transition in $d=1$, but a transition at $k_4>0$ in $d=2$, although - as the authors state themselves - the data are far from convincing. The main difference between our specific model and theirs is that they use very large cells ($\approx$20 particles per cell) and very strong diffusion: the chance of one particle jumping into a cell is comparable or larger than the chance of a chemical reaction in this cell. In our model, in contrast, the number of particles per cell was $\leqq 2$, and the rate of interaction between cells was of the same order of magnitude as the reaction rates within a cell.

As a consequence, even away from any critical point, the correlation length in [21] was so large that fluctuations were coherent over volumes containing very many ($\gtrsim 10^2$) particles. Thus within any reasonably long running time and on any managable lattice size, it seems impossible to reach the critical regime. This is indeed what was found in [21]. Although there it was claimed that no critical behaviour was seen in $d=1$, they did find that the model was bistable (for $d=1$!) for certain rate parameters (private communication). These two statements are of course mutually excluding. As we ex-

pect relaxation times to be even longer in $d=2$, their conclusion in that case seems even less justified.

In realistic applications, it might well be that the parameter choice of [21] is more appropriate. In that case, it might be very hard to observe the critical behaviour, as advocated in the present paper, in any true experiment. In such experiments, one should instead see something like a first order transition. But the sharpness of this transitions is primarily a measure of the size of the cells, not of the total system. This is not what one usually would consider a local interaction model. Also, when more refined experiments would become available, one finally should observe a cross-over to the behaviour described above.

Our conclusion is thus that the second Schlögl model, when treated as a truly local reaction-diffusion system, is an example where fluctuations change drastically the phase structure. It is *not* an example of universality between models with and without detailed balance.

Rather, it suggest another type of universality, comprising all critical points with an absorbing state and a single order parameter in one universality class. This class does not, of course, include multicritical phenomena which also occur in nonequilibrium models. An example resembling a tricritical point occurs in the reaction scheme $2X \to 3X$, $3X \to X$. We have performed some preliminary calculations for this model in 1 dimension, showing indeed a transition with critical behaviour distinctly different from model I.

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