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Cellular automata approach to non-equilibrium phase transitions in a surface reaction model: static and dynamic properties

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Abstract. A cellular automata approach to non-equilibrium phase transitions in a surface reaction model is proposed. This surface reaction model describes a simple adsorption-dissociation-desorption on a catalytic surface. This model exhibits two second-order non-equilibrium phase transitions. The stationary critical exponents for the order parameters β as well as dynamical critical exponents Δ, describing the critical slowing down, are found to be mean-field-like.

1. Introduction

Non-equilibrium dynamical systems can exhibit complicated behaviour, including the formation of dissipative structures, temporal and spatial oscillations, and non-equilibrium phase transitions (Haken 1975). Moreover, there is no first principle theory to describe the properties of such non-equilibrium systems. Accordingly, the study of the behaviour of particular systems may be very useful.

A simple example of a system exhibiting non-equilibrium phase transitions is given by a surface reaction model in which two species can be adsorbed on a surface on which they chemically react. The product of the chemical reaction is desorbed and thus the heterogeneous catalysis process is regenerated. Models for such systems have been proposed by Ziff *et al* (1986) and Schlögl (1972).

Theoretically such systems are usually described in terms of non-linear reaction rate equations for the averaged concentration of each species. However, within this approach, the local fluctuations are totally neglected. In equilibrium statistical mechanics, it is well known that the fluctuations play a crucial role in the vicinity of a second-order phase transition (Ginzburg 1960). Accordingly, it seems important to keep the fluctuations to study the non-equilibrium phase transitions as well.

The cellular automaton (CA) approach offers a way to follow the dynamical evolution and keep track of all the microscopic degrees of freedom. Cellular automaton theory describes a universe consisting of an homogeneous array of cells. Each cell is endowed with a finite number of states and evolves in discrete time according to a uniform local rule (Wolfram 1986). All the cells compute their new state simultaneously. Computation can be performed on very fast special purpose computers with parallel architecture. Moreover, the result of the computation is exact in the sense that no

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rounding errors (which can play an important rule for non-linear dynamics) affect the result.

The goal of this paper is to propose a cellular automata model for the surface reaction problem introduced above. Static and dynamic properties of this CA model are studied. The phase diagram shows two different second-order non-equilibrium phase transitions separating phases with zero rate production of the reactant from phases with finite production rate. It is thus possible to study the static and dynamic critical behaviour of such non-equilibrium phase transitions. The critical exponent β describing the behaviour of the order parameter associated with the two second-order transitions is found to be mean-field-like, i.e. $\beta \simeq 0.5$.

The dynamics of the model is also considered and, in particular, we study how an initial state relaxes towards its stationary value. The corresponding relaxation time τ is shown to diverge in the vicinity of the second-order transition (critical slowing down). The critical exponent Δ characterising this divergence turns out to be mean-field-like, i.e. $\Delta = 1$.

The paper is organised as follows. In § 2, the surface reaction model is defined, and its modelisation in terms of CA given. In § 3 the results of the simulation are quoted. These results are discussed in § 4.

2. The model

The surface reaction model that we consider is similar to the one proposed recently by Ziff *et al* (1986). Differences between the two models will show up through the modelisation in terms of CA. These reaction models are based upon some of the known steps of the reaction $A\text{-}B_2$ on a catalyst surface (for example $CO\text{-}O_2$). The basic steps in heterogeneous catalysis are the following.

(i) A gas mixture with concentrations X_{B_2} of B_2 and $X_A = (1 - X_{B_2})$ of A sits above the surface and can be adsorbed. The surface can be divided in elementary cells. Each cell can absorb one atom only.

(ii) The B species can only be adsorbed in the atomic form. A molecule B_2 approaching an empty cell will be dissociated into two B atoms only if another cell adjacent to the first one is empty. The two first steps correspond to the reactions

$$A \rightarrow A(\text{ads}) \qquad B_2 \rightarrow 2B(\text{ads}).$$

(iii) If two nearest-neighbour cells are occupied by different species they chemically react according to the reaction

$$A(\text{ads}) + B(\text{ads}) \rightarrow AB$$

and the product of the reaction is desorbed. This final desorption step is necessary for the product to be recovered and for the catalyst to be regenerated. However, the gas above the surface is assumed to be continually replenished by fresh material. Thus its composition is constant during the whole evolution.

Note that this model neglects several features which may be present in a real situation. For example, there may be a substantial diffusion and reassociation of the reacting species ($B + B \rightarrow B_2$) or desorption of the unreacted species.

2.1. Cellular automaton realisation

In view of the above description, it seems natural to represent the problem in terms of a two-dimensional cellular automaton.

The cells of the automaton correspond to the elementary cells of the catalyst. Each cell j can be in four different states $|\psi_j\rangle = |0\rangle$, $|A\rangle$, $|B\rangle$ or $|C\rangle$.

$|0\rangle$ corresponds to an empty cell, $|A\rangle$ to a cell occupied by an atom A and $|B\rangle$ to a cell occupied by an atom B. The state $|C\rangle$ describes the conditional occupation of the cell by an atom B. Conditional means that during the next evolution step of the automaton, $|C\rangle$ will become $|B\rangle$ or $|0\rangle$ depending upon the fact that a nearest-neighbour cell is empty and ready to receive the second B atom of the molecule B_2. This conditional state is necessary to describe the dissociation of the B_2 molecules on the surface.

The time evolution of the CA is given by the following set of rules, fixing the state of the cell j at time $t+1$, $|\psi_j\rangle(t+1)$, as a function of the state of the cell j and its nearest neighbours (von Neumann neighbourhood) at time t:

R1. If $|\psi_j\rangle(t) = |0\rangle$ then

$$|\psi_j\rangle(t+1) = \begin{cases} |A\rangle & \text{with probability } X_A \\ |C\rangle & \text{with probability } (1-X_A). \end{cases}$$

R2. If $|\psi_j\rangle(t) = |A\rangle$ then

$$|\psi_j\rangle(t+1) = \begin{cases} |0\rangle & \text{if at least one of the nearest-neighbour cells} \\ & \text{of } j \text{ was in the state } |B\rangle \text{ at time } t \\ |A\rangle & \text{otherwise.} \end{cases}$$

R3. If $|\psi_j\rangle(t) = |B\rangle$ then

$$|\psi_j\rangle(t+1) = \begin{cases} |0\rangle & \text{if at least one of the nearest-neighbour cells} \\ & \text{of } j \text{ was in the state } |A\rangle \text{ at time } t \\ |B\rangle & \text{otherwise.} \end{cases}$$

R4. If $|\psi_j\rangle(t) = |C\rangle$ then

$$|\psi_j\rangle(t+1) = \begin{cases} |0\rangle & \text{if none of the nearest neighbours was} \\ & \text{in the state } |C\rangle \text{ at time } t \\ |B\rangle & \text{otherwise.} \end{cases}$$

Rule R4 expresses the fact that the atoms of B_2 can be adsorbed only if they have been dissociated on two adjacent cells, i.e. if at least two adjacent cells were empty at time $t-1$.

Rules R1 and R4 describe the adsorption-dissociation mechanism while, rules R2 and R3 describe the reaction desorption process. Note that the above rules do not reproduce exactly the physics described above which corresponds to the Ziff model. Indeed, a given cell occupied at time t by a B atom can take part simultaneously in the formation of several AB pairs; the situation is similar for the A atoms, and thus, on the average, there is no bias introduced between the A and B atoms by this mechanism. However, in our model three adjacent B atoms can be adsorbed, a situation not allowed in the Ziff model. These difficulties are intimately related to the fact that all the cells are updated simultaneously in a CA.

As the concentration X_A of the gas varies, different stationary states of the catalysis surface can be foreseen. If X_A is large the surface will be completely covered by the A atoms after some time. The small fraction of B atoms originally adsorbed will rapidly be eliminated through the desorption of AB. The stationary state will consist of a 'poisoned' catalysis of pure A. If X_A is small we have the opposite situation and the stationary state will consist of a 'poisoned' catalysis of pure B. Obviously, once the surface is poisoned by a species, the reaction rate for the creation of AB is zero.

For an intermediate value of X_A, a more interesting situation can occur in which the stationary state is a mixed state composed of a fraction X_A^a of atoms A, a fraction X_B^a of atoms B and a fraction X_0^a of empty cells. The adsorption-dissociation mechanism compensates for the desorption process. The reaction rate is obviously finite in this intermediate region.

It is thus possible to determine the phase diagram of this system, i.e. we can predict what will be the stationary state reached from a given concentration X_A.

It is hopeless to solve this problem analytically and so numerical simulations have been performed; they are discussed in the next section.

3. Results of the numerical simulation

The CA model defined in § 2 has been simulated on a special purpose machine CAM-6 (Toffoli and Margolus 1987) having 256×256 sites with periodic boundary conditions. At time $t = 0$ a randomly prepared mixture of gas with fixed concentration of one species (X_A) sits on top of the surface. All the cells are initially empty (state $|0\rangle$). The evolution starts following the rules defined in § 2. The rules are iterated many times until a stationary state is reached. The stationary state is a state for which the mean coverage fractions X_A^a and X_B^a of atoms of type A or B do not change in time, although microscopically the configurations of the CA can still change. From a few hundred to 25 000 iterations were needed to reach stationarity depending upon the value of X_A. In order to reduce the fluctuations due to the random initial conditions, the results have been averaged over 35 different samples.

The resulting phase diagram is shown in figure 1. For $X_A \geqslant 0.6515 \pm 0.0004 = X_{A1}$ the stationary state is 'poisoned' with A. For $X_A \leqslant 0.5761 \pm 0.0004 = X_{A2}$ the stationary state is poisoned with B. At X_{A1} and X_{A2} one has two non-equilibrium phase transitions

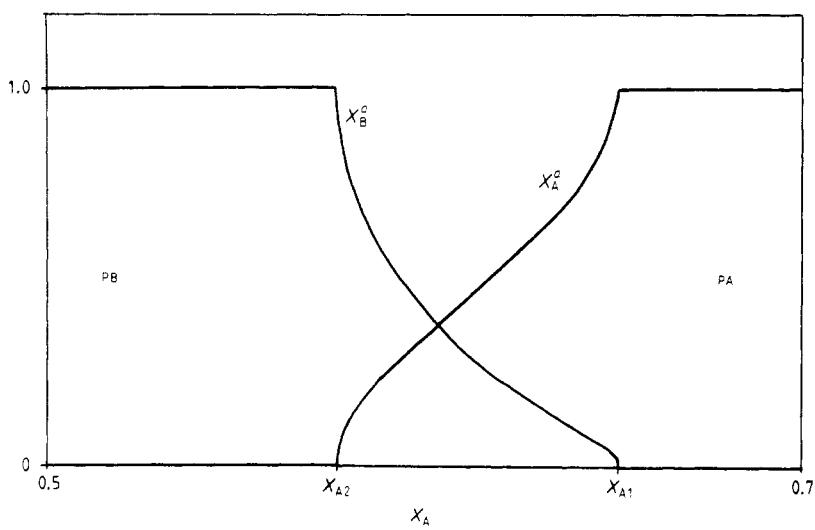

Figure 1. Stationary state phase diagram. X_A is the concentration of the A species of the gas sitting above the catalyst. X_A^a and X_B^a are the fractions of A and B adsorbed, respectively, X_{A1} and X_{A2} are the two critical concentrations. PA and PB denote phases poisoned in A and B, respectively.

in the sense that, in the mixed phase, the coverage concentration varies continuously as a function of X_A at the transitions. We have also determined how the coverage fraction X_A^a goes to zero (or one) near the transition points. The distances from the critical points are determined respectively by the parameters $\varepsilon_1 = (X_{A1} - X_A)/X_{A1}$, $\varepsilon_2 = (X_A - X_{A2})/X_{A2}$.

Fitting the data in the range $8 \times 10^{-4} < \varepsilon_1 < 5 \times 10^{-3}$ one finds that

$$\psi_1 \equiv X_A^a(X_{A1}) - X_A^a(X_A) \sim \varepsilon_1^{\beta_1} \tag{1}$$

with $\beta_1 = 0.55 \pm 0.05$.

ψ_1 can be identified with the order parameter. β_1 is then the stationary critical exponent for the order parameter.

For the second transition, associated to the order parameter ψ_2, one has

$$\psi_2 \equiv X_A^a(X_A) - X_A^a(X_{A2}) \sim \varepsilon_2^{\beta_2}$$

with

$$\beta_2 = 0.45 \pm 0.05 \qquad \text{for } 2 \times 10^{-3} < \varepsilon_2 < 10^{-2}. \tag{2}$$

Although the determination of these exponents is not very precise (the precision could be improved by averaging over more samples), the two values obtained are compatible with a classical or mean-field exponent $\beta = \frac{1}{2}$.

Interesting information can also be obtained concerning the dynamics. In equilibrium statistical mechanics, it is known that a system initially in a non-equilibrium state will decay towards its equilibrium one usually exponentially. The decay is characterised by a relaxation time τ. When approaching a second-order phase transition, this relaxation time diverges (critical slowing down) as

$$\tau \sim \varepsilon^{-\Delta} \tag{3}$$

where ε is the reduced temperature, i.e. the distance from the critical point, and Δ is the dynamical critical exponent. A lot of effort has been devoted to the determination of Δ in several models and attempts have been made to define dynamical universality classes (Hohenberg and Halperin 1977).

A similar situation is present in non-equilibrium phase transitions. Our cellular automaton model allows us to compute the non-equilibrium dynamical critical exponent Δ. The numerical procedure adopted is the following. For a fixed value of X_A, one computes $X_A^a(t)$ or $X_B^a(t)$ depending on the critical point considered. Then the data are fitted with the following decay law:

$$X_\alpha^a(t) = [X_\alpha^a(0) - X_\alpha^a(\infty)] \exp[-t/\tau(X_A)] + X_\alpha^a(\infty) \tag{4}$$

with $\alpha = \mathrm{A}$ or B.

Data are averaged over ten samples in order to reduce the statistical errors. One observes a crossover between two different regimes: an early-time one characterised by a rapid relaxation and a long-time one characterised by the relaxation time $\tau(X_A)$.

Near the transition points, the relaxation times are fitted with the following law:

$$\tau_j(X_A) \sim \varepsilon_j^{-\Delta_j} \tag{5}$$

where $j = 1, 2$ labels the two transitions.

The values obtained for Δ_j are the following. When approaching the transitions from the 'disordered' phase, i.e. the poisoned ones, one finds, for $9\times10^{-4}<\varepsilon_{1,2}<3\times10^{-2}$,

$$\Delta_1 = 0.98 \pm 0.08 \qquad \Delta_2 = 1.03 \pm 0.10. \tag{6}$$

Within the errors bars, both values are compatible with a mean-field value $\Delta = 1$ (Dickman 1987).

When approaching the transitions from the 'ordered' phase, i.e. non-poisoned, one finds

$$\Delta_1 = 1.02 \pm 0.15 \qquad \Delta_2 = 0.84 \pm 0.15 \tag{7}$$

again compatible with the mean-field value.

4. Concluding remarks

The above results show that the cellular automata approach is well suited to studying the surface reaction model. Not only can the phase diagram be obtained with a good precision, but information about some static and dynamical critical exponents can be obtained.

The striking feature is that both static and dynamic exponents are, within the precision of the simulation, mean-field-like. Similar findings, have been obtained in two other problems dealing with non-equilibrium phase transitions. Katz *et al* (1984) have investigated, theoretically and numerically, the stationary non-equilibrium states of a stochastic lattice gas under the influence of a uniform external field. A slightly different version of this model, for which stationary states can be found exactly, has been proposed by van Beijeren and Schulman (1984). They were able to show that static exponents describing the gas-liquid transition were mean-field-like.

On the other hand, Onuki and Kawasaki (1979) have studied the effect of a uniform shearing on a fluid. They showed that, independently of the value of the shearing, the character of the liquid-gas transition changes immediately to become mean-field-like.

What could be the reason in our model for the mean-field character of the non-equilibrium transitions? One important ingredient of our model is the gas mixture sitting above the catalytic surface. This gas has its own independent dynamics. Accordingly, a cell on the surface sees above it, during the time evolution of the CA, a random succession of A and B species (with, however, a given probability). This kind of stirring is efficient enough to suppress the short-range correlation between the cells of the surface, hence explaining the mean-field behaviour.

In view of the known particular examples, it is reasonable to ask the following questions: do dynamical universality classes for these non-equilibrium systems exist and, if the answer is affirmative, what are the characteristics of the universality class with classical exponents? These questions will be addressed in a further publication.

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