Boundary and finite-size effects in lattice models for dynamical phase transitions

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Daniel ben-Avraham†

Clarkson Institute for Statistical Physics (CISP), Physics Department, Clarkson University, Potsdam, NY 13699-5820, USA

Abstract. We study finite-size effects in lattice models for dynamical phase transitions. For the Ziff–Gulari–Barshad (ZGB) model on the Cayley tree, it is shown that the order of the transition from the reactive phase to the monomer-saturated phase depends upon the adsorption rule for dimers at the boundary. We also examine the ZGB model on finite-sized square lattices connected by a single bond. The finite-size effects associated with the first-order and the second-order transitions are markedly different. This phenomenon can be exploited to determine the order of phase transitions numerically, with modest computing requirements. Our findings emphasize the importance of finite-size effects and geometrical constraints in dynamical lattice models. They also help explain the puzzling difference between the behaviour of the ZGB model on percolation clusters and on the Sierpinski gasket.

1. Introduction

Lattice models for dynamical phase transitions are the subject of rapidly growing interest [1–5]. A well known example of both practical and theoretical interest is the model introduced by Ziff, Gulari, and Barshad (ZGB) for the oxidation of carbon monoxide by oxygen on platinum, or palladium [4]. The ZGB lattice model fits experiments better than the classical approaches of rate equations. It exhibits rich kinetic behaviour, including a second-order dynamical phase transition from an absorbing state (lattice saturated with CO) to a reactive steady state, and a first-order transition from the reactive phase to an oxygen-saturated phase. In contrast to equilibrium phase transitions, non-equilibrium (also known as 'dynamical') phase transitions are less well understood and even their classification into universality classes, or which of their properties place them into different classes, are still basic open questions [6].

Indeed, the macroscopic kinetics of lattice models is extremely sensitive to changes in the microscopic details of the models. For example, the monomer–monomer model [7] and the Dollars and dimes (Dd) model [8] represent, stoichiometrically, exactly the same reaction, $A + B \rightarrow AB_\uparrow$. They differ only in that the Dd model includes nearest-neighbour excluded-volume effects for one of the species (the 'Dollars'). This minute change gives rise to a whole new reactive phase [8].

Another manifestation of this extreme sensitivity to detail arises upon variation of the underlying lattices. Studies of the ZGB model on the Sierpinski gasket yield a phase diagram similar to regular two-dimensional space, with one first-order and one second-order phase transition [9]. However, on percolation clusters the first-order transition is replaced by a

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† E-mail address: qd00@craft.camp.clarkson.edu (BITNET).

second-order transition [10]. This difference is puzzling, since for many physical properties, such as elasticity and conductivity, the Sierpinski gasket is known to yield essentially the same physical behaviour as for percolation clusters.

Motivated by this riddle, I explore the effects of some commonly neglected features of the underlying substrate. I first focus on how changes in the reaction rules at the boundary of the lattice influence the kinetics. It is shown that different boundary rules may change the order of dynamical phase transitions. I then study the consequences of connecting finite-size lattices by single bonds. These connecting bonds are analogous to the 'red bonds' in percolation theory [11], which are critical to the transport physics and the elasticity of the clusters. The study of these composite lattices reveals significant differences between finite-size effects in first-order and second-order phase transitions. This suggests a new finite-size scaling technique to determine the order of dynamical phase transitions which requires remarkably modest computing resources.

2. The ZGB model

There have been numerous studies of the ZGB model. Here I will focus on its simplest version of the adsorption-limited case. The CO molecules are represented by 'monomers', A, that need one empty lattice site in order to adsorb. The O_2 molecules are represented by B_2 'dimers' whose adsorption requires two empty sites. The process is schematically written as

$$A + * \rightarrow A* \tag{1a}$$

$$B_2 + ** \rightarrow 2B* \tag{1b}$$

$$A* + B* \rightarrow AB + ** \tag{1c}$$

where '$*$' denotes an active (empty) site and '$A*$' and '$B*$' denote adsorbed particles. The adsorption processes ($1a$) and ($1b$) are attempted with probabilities p and $1-p$, respectively. The reaction ($1c$) is instantaneous. It follows adsorption immediately whenever AB pairs form. The product desorbs freeing two lattice sites.
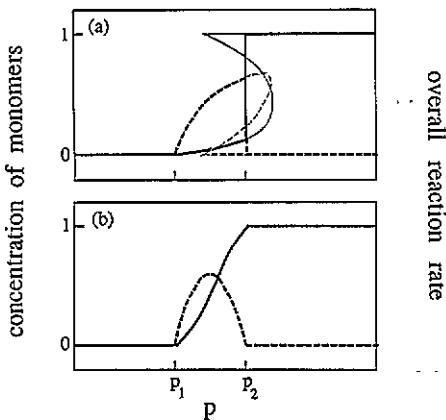

Figure 1. Schematic representation of transitions in the ZGB model in two-dimensional lattices and on the Sierpinski gasket (a), and on percolation clusters (b). Plotted is the coverage of the lattice by monomers (solid lines), and the overall reaction rate (broken lines) as a function of the monomers adsorption probability, p. The metastable loops for the first-order transition at p_2 in case (a) are indicated with thinner lines.

For two-dimensional lattices, a reactive steady state is observed for a range of monomer adsorption probabilities, $p_1 < p < p_2$. For $p < p_1$ ($p_2 < p$) the lattice fills up with B's (A's) and the process stops. The transition from the dimer-saturated phase to the reactive phase is second order, and that from the monomer-saturated phase to the reactive phase is first order. The first-order transition is accompanied by a metastable loop, similar to equilibrium first-order phase transitions, and the production rate is largest at the transition. A similar phase diagram is observed for the ZGB model on the Sierpinski gasket [9]. On percolation clusters, the first-order transition is replaced by a second-order transition and the production rate peaks near the centre of the reactive window [10] (see figure 1).
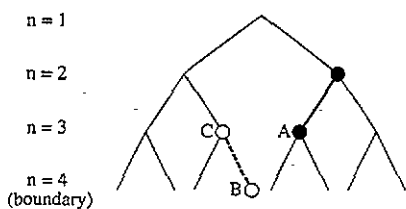

Figure 2. Example of a Cayley tree with $n = 4$ levels. If the first chosen site for adsorption of a dimer is A, the second site may be adsorbed onto any of A's nearest-neighbours with probability $\frac{1}{3}$. When the first site, B, is on the boundary, adsorption onto C (B's only nearest neighbour) is considered with probability p_b.

3. Boundary effects

Normally, in order to minimize finite-size effects, one studies lattice models with periodic boundary conditions. However, from a more realistic perspective, if the simulations are to correspond to small active patches on a catalytic surface, the lattice is truly finite and one should specify the boundary conditions. In the ZGB model, a problem arises with respect to the adsorption of dimers at the boundary: to adsorb a dimer one first picks up a site at random. If the site is empty, one of its z nearest neighbours is randomly chosen (z is the coordination number of the lattice). If the second site is empty, adsorption of the dimer onto the two selected sites takes place. When the first chosen site is at the boundary, it has $z' < z$ nearest neighbours. One can proceed in different ways. For example, make a *forced* choice among the z' sites, with probability $1/z'$, or make a *free* choice—as if there were no boundary—with the usual probability $1/z$.

The effects, if any, of these different possibilities would be emphasized in cases where the boundary sites constitute a finite fraction of all sites, as for example in percolation clusters, or in a Cayley tree. In a Cayley tree, where each site at level n branches into two sites at level $n + 1$, half of all sites are boundary sites at the last layer of the tree. To study the boundary effect, define p_b in the following way: whenever the first chosen site for the adsorption of a dimer is at the boundary, we will consider adsorption onto it and its (only) nearest neighbour with probability p_b (see figure 2). Thus, $p_b = 1$ and $p_b = \frac{1}{3}$ correspond, respectively, to the 'forced' and 'free' boundary conditions discussed above.

In general, we may ask what happens for any $0 \leqslant p_b \leqslant 1$. To answer this question, extensive numerical simulations were performed on Cayley trees consisting of $n = 17$ and $n = 20$ layers (the total number of sites is $2^n - 1$). The larger lattices were used to test for finite-size effects. These were found to be negligible. Most simulations followed the constant coverage (CC) method [12]. In this technique, one finds the average adsorption probability, p, required to maintain a constant concentration of monomers or dimers on the lattice (i.e. the coverage), at the long time asymptotic regime. The CC method enables one

to see the characteristic metastable loop of first-order transitions. Traditional simulations, where p is kept fixed and the average coverage is measured, were performed as a consistency check. Though less accurate than CC [13], the latter technique can locate the actual transition point in first-order transitions.
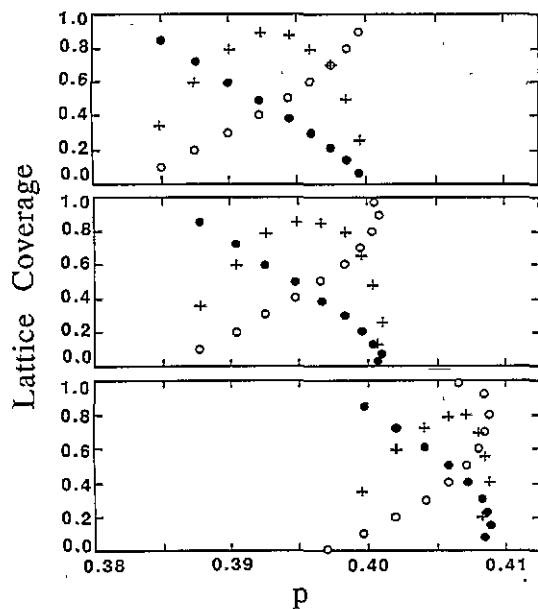

Figure 3. Simulation results for the ZGB model on the Cayley tree. Shown is the lattice coverage by monomers (o) and dimers ($\bullet$), as well as the overall reaction rate (+), as a function of the monomer adsorption probability, p. Plots are for $p_b = \frac{1}{3}$, 0.36, and 0.5 (top to bottom). The metastable loops characteristic to first-order transitions show up first for $p_b > \frac{1}{3}$.

The simulation results show a dramatic dependence on the value of p_b. The three phases observed in regular two-dimensional lattices are also seen on the Cayley tree. The transition from the dimer-saturated phase to the reactive phase is always second order. The transition from the monomer-saturated phase to the reactive phase is second order for $p_b < \frac{1}{3}$, but first-order for $p_b > \frac{1}{3}$. Figure 3 shows typical simulation results for $p_b = \frac{1}{3}$, 0.36, and 0.5. The metastable loops characteristic of first-order transitions develop only as p_b exceeds $\frac{1}{3}$. The width of the metastable loop is rather small, which makes it difficult to detect the first-order transition with the traditional simulation technique. Nevertheless, using this technique the transition was located for $p_b = 0.5$ at $p = 0.408$—a result which is consistent with the loop observed through the CC method.

The production rate is highest around the centre of the reactive window for small p_b, but as p_b increases the maximum moves closer to the monomer-saturated phase. In contrast to the case in regular two-dimensional lattices, the maximum does not coincide with the transition point to the monomer-saturated phase, even when the transition is first order. Finally, the critical values of p which demarcate the reactive window depend strongly upon p_b. As p_b increases, the reactive window shifts to higher values of p and reduces in size: the second-order and first-order transitions are at $p_1 = 0.354$ and $p_2 = 0.388$, for $p_b = 0.1$, and at $p_1 = 0.427$ and $p_2 = 0.432$, for $p_b = 1$.

The boundary probability, p_b, plays the role of a multicritical field analogous to temperature in a liquid–gas transition. At $p_b = \frac{1}{3}$ we have a tricritical point where the separation into two phases (reactive, and monomer-saturated) changes from a continuous (second-order) to a discontinuous (first-order) transition.

From a naive point of view, one expects that these results for the Cayley tree may explain the observed differences between the Sierpinski gasket and percolation clusters. In percolation clusters the boundary constitutes a finite fraction of all sites, and hence it is conceivable that the second-order transition between the reactive and the monomer-saturated phase is an artifact of boundary conditions. However, simulations on percolation clusters using a range of different boundary conditions show the same behaviour (a second-order transition). The explanation actually lies in the effect of the 'red bonds'.
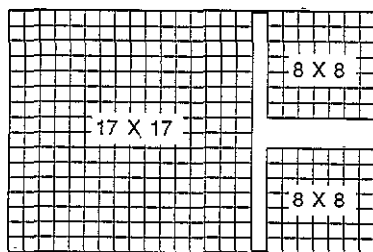

Figure 4. Composite lattice used to study effect of red bonds. The two red bonds connecting the small sublattices to the larger sublattice are indicated by thicker lines.

4. The effect of 'red bonds'

A conspicuous feature of percolation clusters are the 'red bonds'. The red bonds are those bonds that are essential to the connectivity of the clusters: severing a red bond splits a cluster into two disconnected parts. Thus, a percolation cluster may be regarded as a collection of *finite-size* lattices (called 'blobs') that are connected by red bonds. To examine the effect of the red bonds, I have studied finite-size square lattices connected by a single bond (figure 4).

Consider a simulation of the ZGB model on a finite-size square lattice. Because of the finiteness of the lattice there is truly no reactive phase: the system will always evolve to one of the two absorbing states (saturation with either monomers or dimers), at a finite time. However, if the simulation time is limited, the reaction process may still be active as the simulation terminates. Realistically, simulations are finite with regard to both their time extent and the lattice-size. An arbitrary decision must be made as to which part of the data represents the steady state. In the present work the simulations were run up to a time T (one time unit corresponds to one Monte Carlo cycle per lattice site) and the output was averaged over the last 10% of the time.

Generally, one observes finite-size corrections to the ideal thermodynamic limit. If a simulation is performed for a certain value of p within the reactive window (of the thermodynamic limit), a small lattice is likely to saturate sooner than a large lattice. Hence, for a fixed time T the finite-size corrections are more pronounced in small lattices. If the substrate consists of two finite-size lattices connected by a single red bond, we may naively expect that the results will be well approximated by the mass average of the two lattices—as if the lattices were disconnected. Simulations actually show that this is only partly true.

Simulations were performed on 8×8 and 17×17 square lattices (separately), as well as on a composite of these lattices connected by red bonds (figure 4). The time T was fixed at $T = 2400$ in *all* the runs. With some experimentation, we found that this time emphasizes the differences between the finite size-corrections in the two lattice sizes. A typical run requires a few seconds on an IBM-RISC/6000 workstation. This enabled us to perform about 300 runs per data point and to collect all our data in a few CPU hours. All
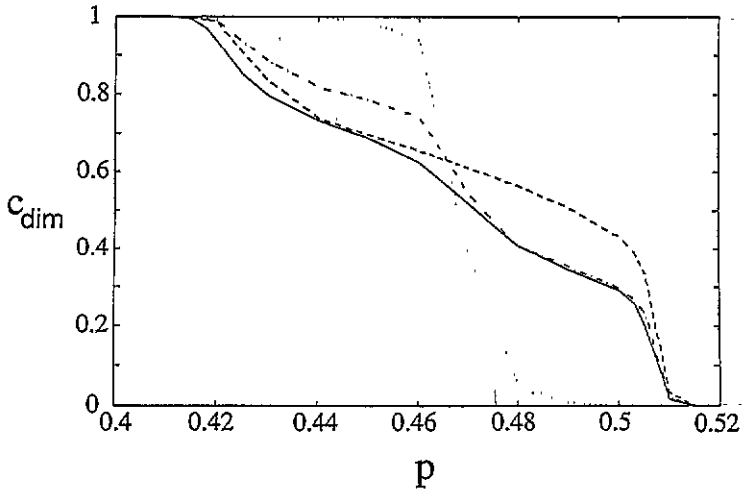
Figure 5. Effect of red bonds. Shown is the lattice coverage by dimers as a function of the monomer adsorption probability, p, for an 8×8 lattice (dotted line), a 17×17 lattice (broken line), their composite lattice of figure 4 (solid line), and the mass average of its three sublattices (broken-dotted line). The mass average agrees well with the composite lattice only near the first-order transition. Near the second-order transition, the composite lattice appears to be effectively larger than the 17×17 sublattice.

simulations were done according to the traditional method, where p is kept constant and data is accumulated for the coverage.

The simulation data are summarized in figure 5. Shown is the concentration of dimers as a function of the monomer deposition probability, p, for the 8×8 lattice, the 17×17 lattice, and the composite lattice of figure 4. The mass-averaged data of the 17×17 lattice and the two 8×8 lattices is drawn for comparison. The finite-size corrections for the smaller 8×8 lattice are significantly larger, as expected. For the larger 17×17 lattice the corrections are smaller; the apparent reactive window is wider, and the transition corresponding to the ideally discontinuous, first-order transition of the thermodynamic limit is sharper.

The data of the composite lattice are well approximated by the mass average near the first-order transition (of the thermodynamic limit). However, near the second-order transition the composite lattice behaves as if it were larger than its separate parts—as if it were the sum of its parts, rather than their average. This difference between the first- and the second-order transitions can be understood in terms of the correlation length. The correlation length is finite for first-order transitions but diverges for second-order transitions. Thus, for first-order transitions the correlation length is short enough that the different parts of the composite lattice cannot communicate effectively across the red bond. The results are then as if the sublattices were disconnected, yielding the mass average. For the second-order transition, the correlation length is large enough that the sublattices can communicate efficiently, even through a single red bond, making the size of the lattice effectively equal to the sum of its parts.

The phenomenon discussed above can be exploited as a method for finding out the order of dynamical phase transitions numerically. Frequently, it is difficult to distinguish between first- and second-order transitions even using prohibitively big lattices and long simulation times. Instead, one could study very small lattices and short simulation times. Comparison

of the apparent transition (as modified by the finite-size effects) on separate lattices to that of the same lattices connected by a red bond would easily reveal the nature of the transition. This method can be carried out with minimal computing power.

We argue that the red bonds are responsible for the transformation of the first-order transition into a second-order transition in percolation clusters. It is plausible that the different 'blobs' are effectively disconnected near the first-order transition, and that their mass-averaged behaviour yields an apparent second-order transition. This hypothesis is confirmed by our simulations of the ZGB model on percolation clusters. Clusters were generated with the Leath algorithm [14] and simulations were performed on the clusters, as well as on the same clusters but with the red bonds blocked (thus effectively disconnecting the cluster into blobs). The results near the transition to the monomer-saturated phase are virtually unaffected by the blocking.

5. Summary and discussion

We have studied some effects arising in dynamical systems from constraints of finite-size: (1) constraints imposed by the boundary of lattices, in the form of special reaction rules, and (2) the effects of connecting finite-size lattices through red bonds. The boundary effects were exemplified by the ZGB model on the Cayley tree, where the adsorption of dimers at the boundary sites is controlled by a probability p_b. This parameter serves as a critical field, analogous to temperature in liquid–gas transitions. The transition from the reactive phase to the monomer-saturated phase is first order for $p_b < \frac{1}{3}$, but second-order otherwise, i.e. there is a tricritical point at $p_b = \frac{1}{3}$. The effect of red bonds was demonstrated for the ZGB model on finite-size square lattices. The simulation results for lattices connected via red bonds are similar to the mass average of the simulation results on the disconnected lattices, near first-order transitions. However, near second-order transitions the red bonds connect the sublattices efficiently, yielding a composite lattice which is seemingly larger than its constituent parts.

Our findings are relevant to the fact that the transition between the reactive phase and the monomer-saturated phase for the ZGB model on the Sierpinski gasket is first order, while it is second order on percolation clusters. Because the boundary sites of percolation clusters constitute a finite fraction of all sites, it is tempting to conclude that boundary effects are responsible for this anomaly. However, we have experimented with different reaction rules at the boundary of percolation clusters, and the transition remained always second order. Moreover, we have simulated the ZGB model on the backbone of percolation clusters. The transition remains second order in spite of the greater similarity of the backbone (over that of the full cluster) to the Sierpinski gasket.

The second-order transition is truly due to the red bonds. The cluster behaves as if it were disconnected into finite-sized 'blobs'. Simulations then yield the mass average of the coverage on the different blobs. This has the effect of smearing the transition, making it seem second order. Indeed, simulations on clusters with the red bonds blocked (effectively disconnecting the blobs) yield the same results as without the blocking, confirming this hypothesis.

A central conclusion of the present work is that we should pay more heed to finite-size effects. In real catalysis systems, reactions frequently take place on small active patches where the boundaries and the averaging over lattices of different sizes may play an important role. We have seen that such effects may even change the nature of phase transitions.

From a theoretical point of view, there remain several interesting open questions. The boundary effect in the Cayley tree provides us with an opportunity to research a tricritical point in a dynamic phase transition. Most second-order transitions in the dynamical systems studied so far belong to the same universality class as directed percolation. Is it also true for the second-order transitions brought about by finite-size effects in the Cayley tree and in clusters connected by red bonds? Previous studies have demonstrated the usefulness of analyzing finite size effects in an ensemble where the stopped processes that have reached saturation are excluded [15]. In this work, we have shown that by including these cases we obtain a powerful technique to determine the order of a transition (the effect of red bonds). In summary, finite-size effects are important in practical systems and may be exploited to yield new theoretical insights and better analysis techniques. Further research in this area is needed.

Acknowledgments

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