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Revisiting the first-order irreversible phase transition of the Ziff–Gulari–Barshad model

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Abstract

The first-order irreversible phase transition (IPT) characteristic of the Ziff–Gulari–Barshad (ZGB) model is studied by means of extensive numerical simulations. Using the constant-coverage method it is found that hysteresis effects hinder the location of the coexistence point. However, the hysteresis loop is unstable against a negligible small external perturbation, allowing the determination of the coexistence point quite accurately. Also, by means of epidemic studies, an existing controversy on the occurrence of scale invariance in the dynamical behaviour of the system at coexistence is resolved. Our findings reconcile the behaviour of the first-order IPTs of the ZGB model with their reversible counterparts.

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The study of non-equilibrium systems has become a challenging subject of interest for many areas of research in physics, chemistry, ecology, catalysis, economics, social sciences etc [1–3]. An intriguing feature of these systems is the occurrence of irreversible phase transitions (IPTs) between an active regime and an absorbing state where the system becomes trapped. Since the work of Ziff, Gulari and Barshad (ZGB) [4], second-order IPTs are well understood since they have been placed either in the directed percolation or parity conserving universality classes [3, 5]. However, due to the lack of experimental feedback on second-order IPTs, the huge activity in the field is mainly of academic–theoretical interest, so it is surprising that, in spite of the existence of experimental evidence on systems undergoing first-order IPTs [6, 7], our understanding of this subject is far from being satisfactory. In fact, based on standard epidemic simulations of the ZGB model, Evans *et al* [8] have claimed that relevant dynamic quantities (e.g. the number of active sites and the survival probability of the epidemics) exhibit power-law behaviour at coexistence. The occurrence of scale invariance at first-order IPTs is certainly a puzzle. A similar controversy has recently arisen in the field of reversible transitions [9]. However, in this case power-law behaviour can be identified as a finite-size effect [9]. Furthermore, the existence of hysteresis, which is a signature of first-order transitions, has, so far, not been theoretically explored in detail in the field of IPTs in spite of available experimental evidence [7].

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The aim of this paper is to present a study of the first-order IPT of the ZGB model based on numerical simulations. Hysteresis effects around coexistence are investigated by means of the constant-coverage (CC) ensemble method as proposed by Ziff and Brosilow [10], while the coexistence point is located using a variant of the spontaneous creation method due to Bidaux *et al* [11]. Furthermore, extensive epidemic simulations allow us to rule out the existence of scale invariance at coexistence.

The ZGB model [4] is a lattice gas adsorption–reaction model, which reproduces some relevant features of the catalytic oxidation of carbon monoxide on a crystal surface. It is assumed that the reaction proceeds according to the Langmuir–Hinshelwood mechanism:

$$\mathrm{CO(g)} + \mathrm{S} \rightarrow \mathrm{CO(a)} \tag{1}$$

$$\mathrm{O_2(g)} + 2\mathrm{S} \rightarrow 2\mathrm{O(a)} \tag{2}$$

$$\mathrm{CO(a)} + \mathrm{O(a)} \rightarrow \mathrm{CO_2(g)} + 2\mathrm{S} \tag{3}$$

where S is an empty site of the lattice, while (a) and (g) refer to the adsorbed and gas phase, respectively. The ZGB model assumes that CO and O_2 molecules randomly hit the surface with probabilities P_{CO} and $P_{\mathrm{O_2}}$, respectively. Due to the normalization condition $P_{\mathrm{CO}} + P_{\mathrm{O_2}} = 1$, the ZGB model has a single parameter, which in most cases is taken as P_{CO}.

In this paper the ZGB model is simulated in a two-dimensional square lattice of size L, assuming periodic boundary conditions. During one Monte Carlo time step (MCS) L^2 sites of the sample are selected at random in order to account for the adsorption–reaction steps described by the set of equations (1)–(3).

Interest in the ZGB model arises because of both its simplicity and its rich and complex irreversible critical behaviour. In fact, in two dimensions and in the asymptotic regime ($t \rightarrow \infty$) the system reaches a non-equilibrium stationary state whose nature solely depends on the parameter P_{CO}. For $P_{\mathrm{CO}} \leqslant P_{1\mathrm{CO}} \simeq 0.389\,857$ ($P_{\mathrm{CO}} \geqslant P_{2\mathrm{CO}} \simeq 0.5255$) the surface becomes irreversibly saturated (poisoned) by O (CO) species. The system also displays a reactive regime between the inactive phases, i.e. for $P_{1\mathrm{CO}} < P_{\mathrm{CO}} < P_{2\mathrm{CO}}$, with a sustained production of CO_2. So, just at $P_{1\mathrm{CO}}$ ($P_{2\mathrm{CO}}$) the ZGB model exhibits second-order (first-order) IPTs between the reactive regime and poisoned states. For additional details of the ZGB model see e.g. [3,4,10].

In order to study hysteresis effects we have employed the CC ensemble [10]. So, in the first step a stationary configuration is achieved using the standard simulation ensemble [4]. Then, the system is switched to the CC ensemble, where the density θ_{CO} is now kept constant. Using the CC ensemble, the effective CO pressure ($\langle P_{\mathrm{CO}} \rangle$) is given by the ratio of CO-adsorption attempts to the total number of adsorption attempts. In simulations, $\langle P_{\mathrm{CO}} \rangle$ is averaged over τ_{A} time steps. Subsequently, θ_{CO} is increased stepwise, allowing the system to relax τ_{R} time steps before each measurement of $\langle P_{\mathrm{CO}} \rangle$. Using this procedure one can obtain the growing coverage branch of the CC loop. After reaching a large CO coverage ($\theta_{\mathrm{CO}} = 0.95$ in this paper), θ_{CO} is now decreased stepwise. In this way the decreasing branch of the CC loop can be recorded. Notice that, in the CC ensemble, θ_{CO} plays the role of the control parameter.

Another approach for the study of IPTs is the epidemic analysis (EA) [8,12,13]. The idea behind an EA is to initialize the simulation using a configuration very close to the poisoned (absorbing) state. This configuration can be achieved by filling the whole lattice with CO, except for a small patch of empty sites in the centre of the sample. Subsequently, during the time evolution of the system the average number of empty sites ($N(t)$) is recorded. Of course, each single EA stops if the sample is trapped in the poisoned state ($N(t) = 0$). Results are averaged over 10^9 different epidemics.

Assuming a power-law behaviour (scaling invariance) the following ansatz is expected to hold [12]:

$$N(t) \propto t^{\eta} \tag{4}$$

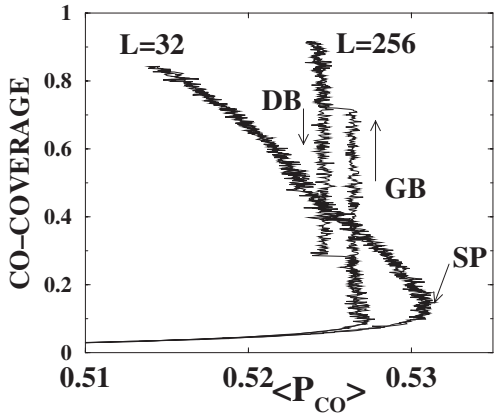

Figure 1. Plots of θ_{CO} versus $\langle P_{CO}\rangle$ obtained using the CC ensemble with $\tau_R = 100$ MCS, $\tau_A = 2000$ MCS and lattices of different size as indicated in the figure. The arrow SP shows the position of the upper spinodal point P_{CO}^{S} for the sample of size $L = 32$. Arrows pointing up and down show the GB and DB θ_{CO} of the hysteresis loop, respectively.

where η is a dynamic critical exponent. The validity of equation (4) for the second-order IPT observed in the ZGB model is supported by extensive numerical simulations [13]. In fact, this IPT belongs to the directed percolation (DP) universality class [12, 13]. The observation of a power-law behaviour for second-order IPTs is in agreement with well established ideas developed in the study of equilibrium (reversible) phase transitions: scale invariance reflects the existence of a diverging correlation length at criticality.

Figures 1 and 2 show plots of θ_{CO} versus $\langle P_{CO}\rangle$ obtained by means of the CC method and using lattices of different size. Due to the overlapping between both the growing branches (GBs) and decreasing branches (DBs) of the CC loop, one concludes that in the ZGB model hysteresis effects are absent for small lattices (e.g. for $L \leqslant 64$ in figure 1). However, hysteresis loops can be distinguished for larger lattices (e.g. for $L = 256$ and 1024 in figures 1 and 2, respectively). Notice that coexistence between the poisoned state and the reactive regime is observed for a wide range of θ_{CO} values (see figure 2).

The CC method allows us to locate the upper spinodal point P_{CO}^{S} as shown in figure 1 for the sample of size $L = 32$. It is found that the upper spinodal point depends on the lattice size. Then, the L-dependent spinodal points defined as $P_{CO}^{S}(L)$ are plotted versus L^{-1} in order to obtain the asymptotic value in the infinite-size limit (see figure 3). The extrapolation yields $P_{CO}^{S}(\infty) = 0.5270(5)$. This result can be compared with values previously reported for finite lattices, e.g. $P_{CO}^{S}(L = 256) \simeq 0.527$ [10] and $P_{CO}^{S}(L = ?) \simeq 0.5285$ [8].

Also, the average CO pressure corresponding to both the CO GB and DB of the loops (given by P_{CO}^{GB} and P_{CO}^{DB}, respectively) can be evaluated and plotted versus L^{-1}, as shown in figure 3. Since coexistence is observed for a wide range of θ_{CO} values, at least for large lattices (see e.g. figures 1 and 2), branches can be located with great accuracy. Furthermore, the position of the branches does not sensitively depend on the lattice size, as shown in figure 3. So, averaging over the larger samples we obtain $P_{CO}^{GB} \cong 0.526\,41(1)$ and $P_{CO}^{DB} \cong 0.524\,67(3)$.

For systems in equilibrium, the location of the coexistence point can be found using thermodynamic integration [14], but for IPTs one lacks any method based on energetic arguments. One (naive) approach is to assume that the coexistence point is in the middle of the hysteresis loop, i.e. $P'_{2CO} = 0.5255(8)$. However, a more reliable method can be envisioned by analysing the stability of both branches of the loop due to the introduction of a

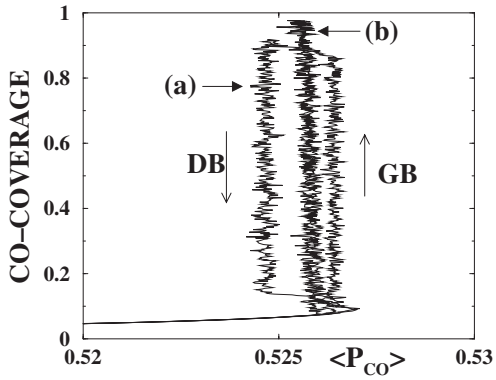

Figure 2. Plots of θ_{CO} versus $\langle P_{CO}\rangle$ obtained using the CC ensemble with $\tau_R = 100$ MCS, $\tau_A = 2000$ MCS and lattices of size $L = 1024$. Curve (a) corresponds to the standard ZGB model as in figure 1. Arrows pointing up and down show the GB and DB θ_{CO} of the hysteresis loop, respectively. In curve (b) the collapse of both branches into a single vertical curve is due to the addition of a small desorption rate of CO given by $R_D = 10^{-6}$.

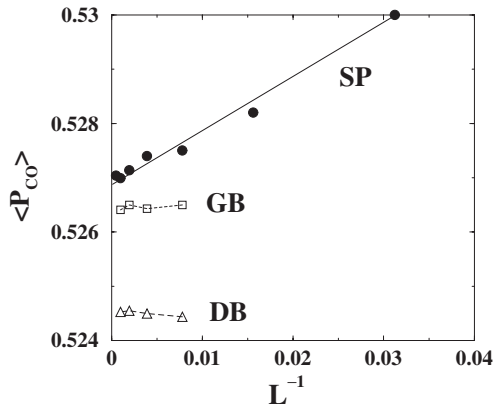

Figure 3. Plots of the upper spinodal point P_{CO}^{S} (● SP), P_{CO}^{GB} (□ GB) and P_{CO}^{DB} (△ DB) versus L^{-1}. More details in the text.

negligible small rate of CO desorption (R_D). This procedure is equivalent to the spontaneous creation method early introduced to study first-order IPTs [11]. Taking $R_D = 10^{-6}$, it is observed that, while the first-order nature of the IPT remains, both branches become unstable against the perturbation and collapse into a single vertical line at $P_{2CO} = 0.525\,83(9)$, which we identify with the coexistence point (figure 2). This figure can be compared with the best available value reported by Ziff and Brosilow [10] given by $P_{2CO} \cong 0.525\,60 \pm 0.000\,01$. This small error bar reported for the coexistence point may be optimistic in view of the lattice size used in that work.

Second-order critical points are often obtained very accurately by means of the EA [13]. However, we have found that this method is not suitable for locating first-order coexistence points. Therefore, in order to carry out a reliable EA an accurate determination of the coexistence point is necessary. As shown above P_{2CO} has been evaluated by using both the CC ensemble and the spontaneous creation method. Then, we are now in a position to perform an EA. Results obtained for $P_{CO} \geqslant P_{CO}^{DB}$ show pronounced curvature, with clear evidence of a cut-

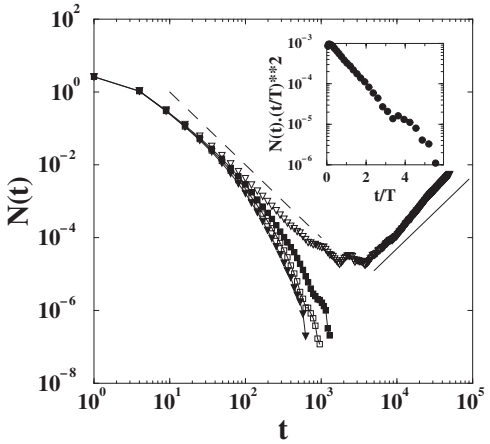

Figure 4. Log–log plots of the number of vacant sites $N(t)$ versus t for EA of the ZGB model. Results averaged over 10^9 different runs (▼ $P_{CO}^{GB} = 0.526\,41$, ■ $P_{CO}^{DB} = 0.524\,67$, □ $P_{2CO} = 0.525\,54$, ▽ $P_{CO} = 0.523\,45$). For the latter case, two straight lines have been drawn for the sake of comparison: the dashed one with $\eta^{eff} = 2$ and the full one with slope 2, respectively. The inset shows a semi-logarithmic plot of $N(t)(T/t)^{-2}$ versus t/T with $T = 183$, according to equation (5), obtained at P_{2CO}.

off (see figure 4). So, for the ZGB model at coexistence $N(t)$ does not exhibit scale invariance as observed in second-order IPT. Our finding is in contrast with previous results claiming power-law and scaling behaviour [8]. The difference may be due to the huge statistics used in this paper where results are averaged over 10^9 different runs. For $P_{CO} < P_{CO}^{DB}$, $N(t)$ exhibits a pseudo-power-law behaviour over many decades with an effective exponent $\eta_{eff} \cong 2.0 \pm 0.1$ (see figure 4). Power-law behaviour at a first-order transition can also be observed when this point is in the neighborhood of a second-order critical point [15], however in the present case this possibility can be ruled out[1]. Furthermore, after a long time, a successful epidemic spreading may prevail causing $N(t)$ to suddenly grow as $N(t) \propto t^2$, as shown in figure 4, indicating a spatially homogeneous spreading. In order to understand the behaviour of $N(t)$ at coexistence we propose a variation of equation (4) given by

$$N(t) \sim (t/T)^{-\eta_{eff}} \exp(-t/T) \tag{5}$$

where T sets a characteristic time scale. Our proposal is validated in the inset of figure 4. A regression analysis gives for the only free parameter $T \cong 183 \pm 3$, initializing the epidemic with an empty patch of three sites. Epidemics initialized with patches of sizes six and nine sites (not shown here) exhibit the same behaviour after a short transient of a few MCS, so the behaviour of $N(t)$ at coexistence is characterized by a pseudo-power-law behaviour for short times ($t < T$) that crosses over to an asymptotic exponential decay for larger times.

In summary, we have performed an extensive numerical study of the first-order IPTs of the ZGB model. In contrast to previous belief, this irreversible transition shares several features with its equilibrium counterpart, namely (i) hysteresis is absent from small samples but becomes clearly evident in large lattices and (ii) the occurrence of a power law (scale invariance) in the dynamic behaviour at coexistence, as measured by means of EA, can be

[1] Since the transition is to a unique absorbing state, any possible second-order IPT belong to the DP universality class, such as $N(t) \propto t^{\eta}$ with $\eta \approx 0.214$ in two dimensions. Then, in the neighborhood of a DP point, a growing DP short time behaviour followed by a crossover to the true asymptotic behaviour is expected. However, $N(t)$ exhibit a decreasing short time behaviour which is in contrast to the above statement.

safely ruled out. We expect that these numerical findings will be helpful for developing a theoretical framework in the field of first-order IPTs.

Acknowledgments

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