Higher-order moments at the critical point of the Ziff-Gulari-Barshad model

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We studied the continuous phase transition between the active and the absorbing state of the Ziff-Gulari-Barshad (ZGB) model. Through Monte Carlo simulations we determined all the moments of the order parameter up to fourth order and their ratios at the critical point. We show that the ratios we found are in agreement with those of the contact and pair contact processes in two dimensions, which give support to the idea that the ZGB model is in the directed percolation universality class in (2+1) dimensions.

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I. INTRODUCTION

In this paper we determine the moment ratios at the critical point of the Ziff-Gulari-Barshad (ZGB) model in two dimensions. Our strategy follows the same reasoning as advanced by Dickman and Leal da Silva in their recent two papers [1,2]. In these works they chose suitable ratios between moments of the order parameter of the *A* model [3] in one dimension, and the contact process [4] and pair contact process [5,6] in one and two dimensions. After calculating the critical exponents and the moment ratios at the critical point for all these models, they concluded that they belong to the appropriate one- or two-dimensional DP universality class. We will show that our calculations for the moment ratios of the ZGB model, extrapolated to large lattice sizes, agree with those found by these authors for the models they studied in two dimensions.

Let us briefly present the ZGB model. This model, proposed by Ziff, Gulari, and Barshad [7], is the simplest one used to explain the irreversible oxidation of CO molecules on a catalyst surface. In the ZGB surface reaction model, molecules of CO and O_2 are adsorbed on a square lattice, according to their partial pressures in the gaseous phase. The whole process follows the Langmuir-Hinshelwood mechanism and the following three steps must be considered:

(1) $\mathrm{CO}(g)+V\rightarrow\mathrm{CO}(a)$,
(2) $\mathrm{O_2}(g)+2V\rightarrow 2\mathrm{O}(a)$,
(3) $\mathrm{CO}(a)+\mathrm{O}(a)\rightarrow\mathrm{CO_2}(g)+2V$,

where the labels *a* and *g* denote adsorbed and gaseous particles, respectively, and *V* is a vacant site. Steps (1) and (2) describe the adsorption of the molecules CO and O_2, respectively, and the third step represents the reaction between the adsorbed species to form the CO_2 molecule. When the O_2 molecule arrives at the surface it dissociates completely. The reaction occurs instantaneously when a CO molecule sees a nearest-neighbor O atom. To describe the whole process we need only a single parameter, which is taken as the relative adsorption rate of CO molecules, denoted by y_{co}. The Monte Carlo simulations performed by these authors show the appearance of active and nonactive states in the phase diagram. For instance, for $y_{\mathrm{co}}\leqslant y_1$, an O poisoned state is observed, and for $y_{\mathrm{co}}\geqslant y_2$, a completely poisoned CO state is found. On the other hand, for $y_1<y<y_2$, a reactive steady state is formed, with a nonzero number of vacant sites. In this paper we focus our attention on the continuous transition that occurs at y_1. The remainder of this paper is organized as follows: in Sec. II, we present the model and the moment ratios of interest, and in Sec. III, we describe the results of Monte Carlo simulations and also present our conclusions.

II. MODEL AND THE MOMENT RATIOS

Near the continuous phase transition at y_1, we choose the fraction of vacant sites $\langle n_v\rangle$ as the order parameter for the ZGB model. Different from the usual continuous transitions in spin systems, where up-down symmetries are present, the order parameter for the ZGB model can only be zero or positive. In this way, odd moments must be included if we are interested in a proper expansion in cumulants. We considered all the moments up to fourth order, which are defined by $m_k=\langle n_v^k\rangle$, with $k=1,2,3,4$, and the second-order cumulant defined by $Q_2=m_2-m_1^2$. In order to determine these moments, we first need to locate the critical point y_1. When we try applying finite-size scaling arguments to the ZGB model, we must be careful, due to the existence of absorbing states. For a finite sample very near to the critical point, the system always poisons. Indeed, to circumvent these problems, we study the quasistationary states of a large number of surviving samples in order to properly evaluate the statistical means of interest. The transient times depend on the linear size *L* of the system and on the distance from the critical point y_1, which is measured by the parameter $\Delta=y_{\mathrm{co}}-y_1$. Then, for large *L* and small Δ, the quasistationary order parameter can be described by the equation

$$m_1(\Delta,L)\propto L^{-(\beta/\nu_\perp)}f(\Delta L^{1/\nu_\perp}), \tag{1}$$

where the scaling function $f(x)\propto x^\beta$ for large values of *x*. β is the order-parameter critical exponent and $\nu_\perp$ is the critical exponent associated with the spatial correlation length. At the critical point we can write that

$$m_1(0,L)\propto L^{-(\beta/\nu_\perp)}. \tag{2}$$

For the calculation of the higher moments, it is interesting to introduce the probability distribution $P(n_v,L)$ for the density of vacant sites at the critical point. In this way the *k*th moment of the order parameter can be computed by

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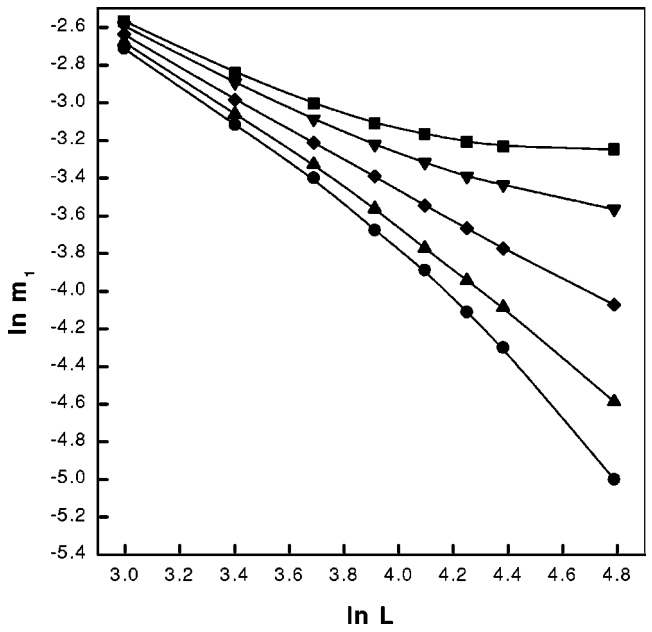

FIG. 1. Stationary density of vacant sites vs system size for $y_{co}=0.385$, 0.386, 0.3875, 0.389, and 0.390 (from bottom to top). The critical point is determined from the straight line.

$$m_k = \int_0^1 n_v^k P(n_v, L)\, dn_v = I_k L^{-(k\beta/\nu_\perp)}, \tag{3}$$

where I_k is independent of L in the large-L limit [8]. Therefore, for large values of L, we can form some ratios between powers of the moments such as

$$\frac{m_k^r}{m_l^s} \propto L^{-(\beta/\nu_\perp)(kr-ls)}. \tag{4}$$

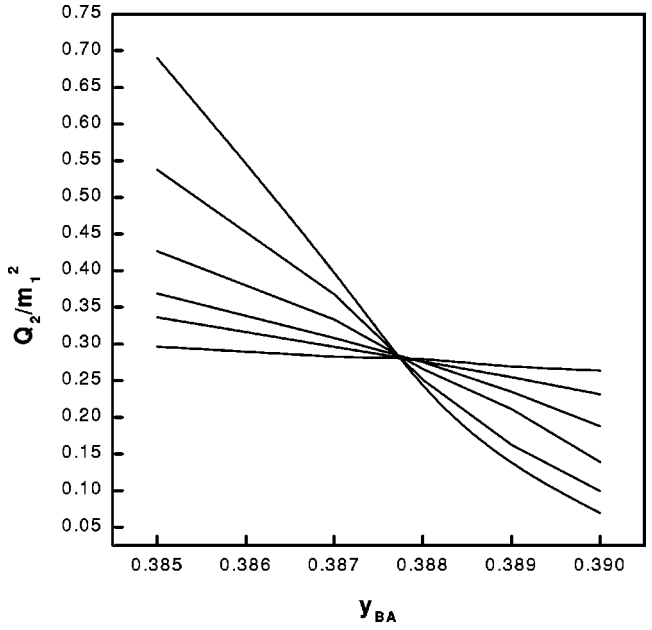

FIG. 2. Ratio Q_2/m_1^2 vs y_{co}. System sizes $L=20$, 40, 60, 80, 100, and 120 are in order of increasing steepness.

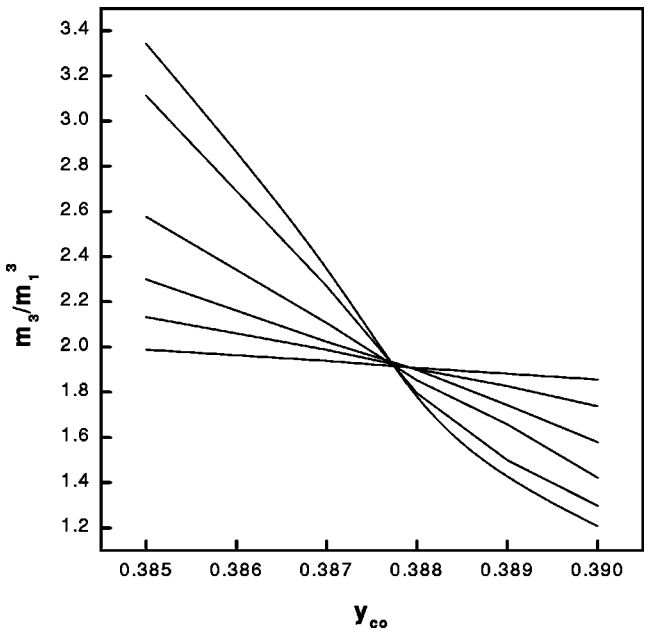

FIG. 3. Ratio m_3/m_1^3 vs y_{co}. System sizes $L=20$, 40, 60, 80, 100, and 120 are in order of increasing steepness.

If $kr=ls$, this ratio is independent of L at the critical point. Then, we expect that plots of these ratios, or a combination of them, as a function of y_{co}, must intercept themselves at the critical point for any value of L. In particular, we have considered the following five ratios at the critical point of the ZGB model: Q_2/m_1^2, m_4/m_2^2, m_3/m_1^3, m_3/m_1m_2, and m_2/m_1^2.

III. RESULTS AND CONCLUSIONS

We have performed simulations for the ZGB model on a square lattice with linear dimensions ranging from $L=10$ to $L=120$. We started all simulations with an empty lattice and used periodic boundary conditions. In order to speed the simulations we have kept a list of empty sites where the adsorption of the species CO and O_2 are made. For each value of the deposition rate y_{co} of the CO molecules, we generate a random number to know what molecule will be deposited in the next step. If we choose CO, a site of the list is chosen at random for deposition, while for the deposition of O_2, we need to choose at random a pair of nearest neighbors from the list. After any trial of the deposition of a given species we investigate its neighborhood looking for reactions, and an update of the list is immediately performed.

First, we need to locate the critical point of the model. In this way we examine the stationary values of the density of vacant sites m_1 for different lattice sizes. For instance, for the lattice size $L=20$, the averages were computed for 1.5×10^5 independent samples, and we considered a time interval between 300 to 500 MC's where the samples exhibited a quasistationary behavior. On the other hand, for the largest lattice size, $L=120$, we took 1.0×10^3 samples, and the time interval for the quasistationary states was 1.75×10^4 until 1.80×10^4. In Fig. 1 we exhibit a log-log plot of the density m_1 vs L. From this plot, we observe that the best fit to the

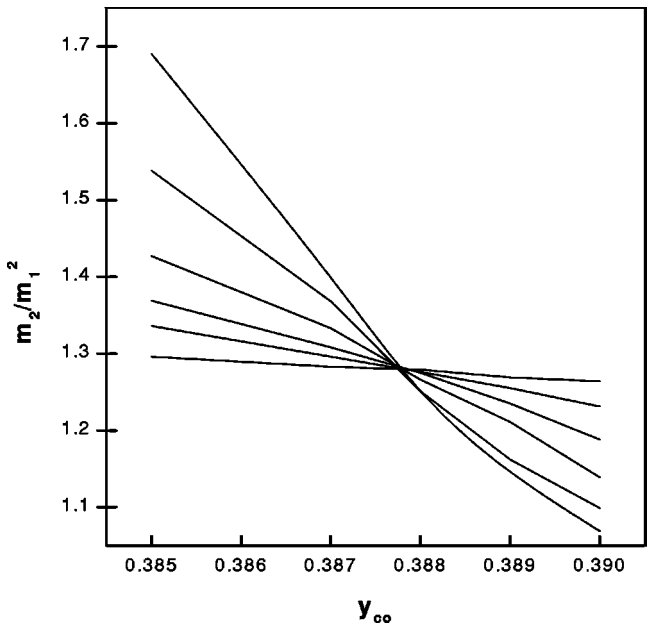

FIG. 4. Ratio m_2/m_1^2 vs y_{co}. System sizes $L=20$, 40, 60, 80, 100, and 120 are in order of increasing steepness.

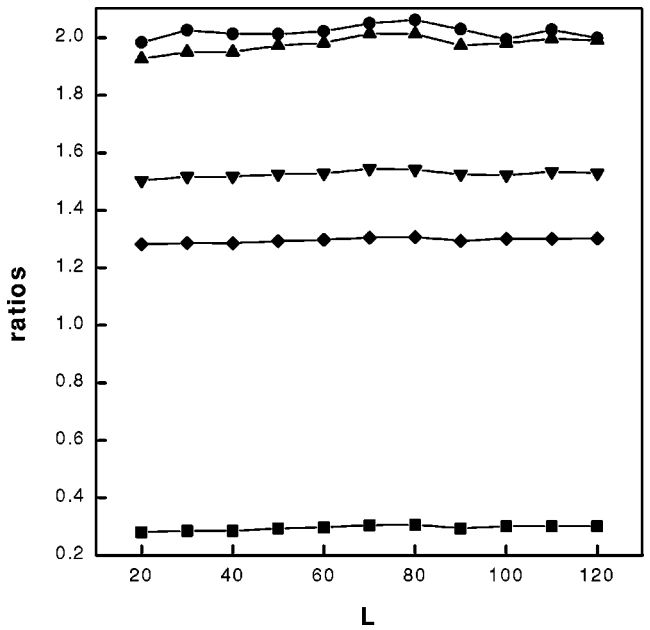

FIG. 5. Order-parameter moment ratios for the ZGB model at the critical point. Squares: m_2/m_1^2; diamonds: m_2/m_1^2; down triangles: m_3/m_1m_2; up triangles: m_3/m_1^3; and circles: m_4/m_2^2.

power law given by Eq. (2), corresponds to a critical value of $y_1=0.3875\pm0.0002$. The curves for $y_{co}=0.3860$ and $y_{co}=0.3890$ clearly depart from the straight line behavior. For the straight line at the critical point $y_1=0.3875$, we obtained the exponent ratio $\beta/\nu_\perp=0.804\pm0.008$. This value appears to be in good agreement with that foreseen by Grinstein *et al.* [9] for directed percolation in $(2+1)$ dimensions, where $\beta_o=0.63\pm0.03$ and $\nu_\perp=0.85\pm0.05$.

Figure 2 represents the plot of the ratio Q_2/m_1^2 as a function of y_{co} for the lattice sizes $L=20,40,\ldots,120$. We clearly see that all the curves cross themselves around the critical point $y_1=0.3875$, as to be expected. The same behavior is observed for all the other moment ratios that we have considered, as we see in Figs. 3 and 4, where we have plotted, for example, the ratios m_3/m_1^3 and m_2/m_1^2 vs y_{co}, respectively.

Finally, in Fig. 5, we exhibit our results for all the moment ratios, calculated at the critical point y_1, versus the lattice size L. We observe only a very slight dependence of the moment ratios on the lattice size L. A linear extrapolation of these ratios for $L\to\infty$, taking only the four largest lattice sizes, i.e., $L=90$, 100, 110, and 120, gives the following results for the ratios: $Q_2/m_1^2=0.33\pm0.01$, $m_4/m_2^2=1.95\pm0.09$, $m_3/m_1^3=2.06\pm0.03$, $m_3/m_1m_2=1.55\pm0.02$, and $m_2/m_1^2=1.33\pm0.01$. As we note these ratios are in close agreement with those found in Refs. [1] and [2], for the contact and the pair contact process models, respectively.

In summary, we have investigated the critical properties of the ZGB model at the continuous phase transition. We have determined the critical point and the corresponding static critical ratio between the exponents β and $\nu_\perp$. We have also computed some moment ratios of the order parameter at the critical point. We have seen that they are in agreement with similar ratios found for the contact and the pair contact processes in two dimensions. Our calculations for the ZGB model corroborate all the previous reasoning that it is in the same universality class of the directed percolation in $(2+1)$ dimensions.

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