Critical behaviour of a surface reaction model with infinitely many absorbing states

Iwan Jensen

Department of Mathematics, The University of Melbourne,
Parkville, Victoria 3052, Australia.
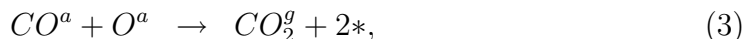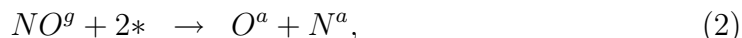e-mail: iwan@mundoe.maths.mu.oz.au

February 1, 2008

Abstract

In a recent letter [J. Phys. A **26**, L801 (1993)], Yaldram *et al* studied the critical behaviour of a simple lattice gas model of the CO-NO catalytic reaction. The model exhibits a second order nonequilibrium phase transition from an active state into one out of infinitely many absorbing states. Estimates for the critical exponent β suggested that the model belongs to a new universality class. The results reported in this article contradict this notion, as estimates for various critical exponents show that the model belongs to the universality class of directed percolation.

PACS Numbers: 05.70.Ln, 05.50.+q, 64.90.+b

Nonequilibrium phase transitions occur in many models studied in physics, chemistry, biology or even sociology. A special group of models, that have attracted a great deal of interest in recent years, exhibit a continuous transition into an absorbing state. The best known examples are probably directed percolation (DP) [1]–[4], Reggeon field theory [5, 6], the contact process [7]–[9], and Schlögl's first and second models [10]–[13]. Extensive studies of these and many other models [14]–[22] with a *unique* absorbing state have revealed that they belong to the same universality class. This provides firm support for the conjecture that continuous transitions into a unique absorbing state generically belong to the DP class [12, 13].

For models with multiple absorbing states the situation is not so simple. Some studies of two-dimensional surface reaction models yield critical exponents different from those of directed percolation in (2+1)-dimensions [23, 24]. However, the pair contact process (PCP) and dimer reaction (DR) model (in one dimension) clearly belongs to the DP universality class [25, 26], at least as far as the *static* critical behaviour is concerned. In all of these models the number of absorbing configurations grows exponentially with system size. However, all of the absorbing configurations are characterized by the vanishing of a unique quantity, e.g., the number of particle pairs in the PCP or in other cases the [23, 24] number of nearest neighbor vacancy pairs.

Recently, Yaldram *et al.* [27], studied the critical behaviour of a simple lattice model of the CO-NO catalytic reaction in which $CO + NO \rightarrow CO_2 + \frac{1}{2}N_2$. Schematically the reaction steps are given as:

$$CO^g + * \rightarrow CO^a, \tag{1}$$

$$NO^g + 2* \rightarrow O^a + N^a, \tag{2}$$

$$CO^a + O^a \rightarrow CO_2^g + 2*, \tag{3}$$

$$N^a + N^a \rightarrow N_2^g + 2*, \tag{4}$$

where the superscript *g (a)* refers to a molecule in the the gas fase (adsorbed on the surface) and $*$ marks an empty site. The catalytic surface is modelled by a two-dimensional triangular lattice. The rules of the computer algorithm are quite simple, with probability p a CO molecule is adsorbed on an empty site and with probability $1 - p$ NO adsorption is attempted. Since NO dissociates upon adsorption it requires a nearest neighbour pair of empty sites. In the simulations this is done by first chosing an empty site at random and then chosing one of the six nearest neighbours randomly, if the neighbour is empty O is placed on the original site and N on its neighbour. After each adsorption the nearest neighbours

are checked (in random order) and CO+O reacts to form CO_2 which leaves the surface at once, likewise N+N forms N_2 which desorbs immediately. It is thus obvious that any state without empty sites is absorbing. All processes depend on the presence of empty sites so an efficient algorithm uses a list of these. After each attempted adsorption the time variable is incremented by $1/N_e$, where N_e is the number of empty sites prior to the attempt, thus making each time step equal to (on the average) one attempted update per lattice site. The algorithm outlined above differs from that used by Yaldram *et al.* in one aspect, when NO adsorbs they choose a *pair* of empty sites at random, whereas I choose one empty sites and a nearest neighbor and only adsorb NO if the nearest neighbor is empty. This makes NO adsorption less likely in my algoritm. However, one would expect this merely to lead to a change in the location of the phase transitions *not* to a change in the critical behaviour. Computer simulations by Yaldram *et al.* [27] shows that when $p < p_1$ the system always enters an absorbing state in which the lattice is covered by a mixture of O and N (but off course without any nearest neigbour pairs of N). Note that the symmetry of the lattice prevents a CO from being surrounded by N, as some of these N would have to be nearest neighbours and thus react. The number of absorbing configurations grows exponentially with system size. Note also that an absorbing configuration, though not unique, is characterized by the vanishing of the number of empty sites. At p_1 the model exhibits a *continuous* phase transition into an active state in which the catalytic process can prodeed indefinetely. Finally when p exceeds a second critical value p_2 the model exhibits a *discontinuous* phase transition into a CO and N covered state. The phase diagram of the CO-NO reaction model is thus very similar to that found in various similar catalytic model [14, 23, 24]. Near the critical point p_1 one would expect the concentrations ρ_X of various lattice sites X ($X = $ O, N, CO, or an empty site) to follow simple power laws,

$$\rho_X - \rho_X^{sat} \propto (p - p_1)^{\beta_X}, \qquad (5)$$

where ρ_X^{sat} is the saturation concentration. Note that the saturation concentration for empty sites and CO is zero, whereas it is non-zero for O and N. Yaldram *et al.* [27] found that $p_1 = 0.185(2)$, where the figure in parenthesis is the uncertainty in the last digit, and $\beta_X = 0.20 - 0.22$. The estimates for β_X are much smaller that the value $\beta = 0.592(10)$, obtained using the scaling relation $\beta = \delta\nu_\parallel$ [11] with $\delta = 0.460(6)$ and $\nu_\parallel = 1.286(5)$ [28], for directed percolation in (2+1)-dimensions. This could indicate that the CO-NO model belongs to a new universality class. However, the uncertainty in the estimate for p_1 is quite large, especially considering that the β estimates are obtained using values of $p - p_1$ between 0.01 and 0.001, which overlaps the error estimate for p_1. Moreover, the lattice sizes (40×40) used in the simulations are very small. Actually for such small lattice

sizes one would expect finite-size effects to be quite prominent. All in all I think there is ample reason to doubt the validity of the exponent estimates obtained by Yaldram *et al.*.

In this article I report the results of extensive simulations of the CO-NO model using time-dependent simulations and finite-size scaling. The general idea of time-dependent simulations is to start from a configuration which is very close to the absorbing state, and then follow the "average" time evolution of this configuration by simulating a large ensemble of independent realisations. This method is straight forward and very successful for models with a unique absorbing state [11, 15, 18, 19, 28]. For models with multiple absorbing state the situation is more intricate, as a recent study [26] revealed that the *dynamic* critical exponents predicted via time-dependent simulations depend upon the choice of initial configuration. However, two important facts emerged from this study, first of all the predictions for the location of the *critical point* was allways correct, and secondly if one uses an initial configuration reminiscent of a *typical* absorbing configuration the predictions for the dynamical critical exponents coincide with those expected from the static critical behaviour. A recent more thorough study by Mendes *et al.* [29] have confirmed this picture and led to a generalized scaling ansatz for models with multiple absorbing states. In this study I generate the initial configuration by simulating the CO-NO model on a 128×128 lattice (with periodic boundary conditions) at the value of p under investigation until it enters an absorbing state. An off-set (x, y) is then chosen randomly on this lattice. Hereafter the configuration is mapped cyclically onto a larger (512×512) lattice such that (x, y) is at the origin of the larger lattice. The particle at position (i, j) on the large lattice is the same as the particle at position $(i+x \bmod 128, j+y \bmod 128)$ on the small lattice. Hereafter a pair of empty sites is placed at the origin. The size of the large lattice ensures that the cluster of empty sites grown from the seed at the origin never reaches the boundaries of the lattice. We thus start in a configuration close to an absorbing state (just two sites are open) and it should be close to a typical absorbing state of the infinite system. For each such configuration I simulated 5000 independent samples and typically 50–100 independent configurations for a total of 250-500,000 samples. Each run had a maximal duration of 2000 time steps, but most samples enters an absorbing state before this limit is reached. As usual in this type of simulation I measured the survival probability $P(t)$, the average number of empty sites $\bar{n}(t)$, and the average mean square distance of spreading $\bar{R}^2(t)$ from the origin. Notice that $\bar{n}(t)$ is averaged over all runs whereas $\bar{R}^2(t)$ is averaged only over the surviving runs. In accordance with the scaling ansatz for models with a unique absorbing state [11, 28] it follows that these quantities have the following scaling form,

4

$$P(t) \quad \propto \quad t^{-\delta}\Phi(\Delta t^{1/\nu_\|}), \tag{6}$$

$$\bar{n}(t) \quad \propto \quad t^{\eta}\Psi(\Delta t^{1/\nu_\|}), \tag{7}$$

$$\bar{R}^2(t) \quad \propto \quad t^{z}\Theta(\Delta t^{1/\nu_\|}), \tag{8}$$

where $\Delta = |p - p_1|$ is the distance from the critical point, and $\nu_\|$ is the time-like correlation length exponent. If the scaling functions Φ, Ψ, and Θ are non-singular at the origin it follows that $P(t)$, $\bar{n}(t)$, and $\bar{R}^2(t)$ behave as power-laws at p_1 with critical exponents $-\delta$, η, and z, respectively, for $t \to \infty$. Generally one has to expect corrections to a pure power law behaviour so that, e.g., $P(t)$ is more accurately given by [28]

$$P(t) \propto t^{-\delta}(1 + at^{-1} + bt^{-\delta'} + \cdots) \tag{9}$$

and similarly for $\bar{n}(t)$ and $\bar{R}^2(t)$. More precise estimates for the critical exponents can be obtained if one looks at local slopes

$$-\delta(t) = \frac{\log[P(t)/P(t/m)]}{\log(m)}, \tag{10}$$

and similarly for $\eta(t)$ and $z(t)$. In a plot of the local slopes vs $1/t$ the critical exponents are given by the intercept of the curve for p_1 with the y-axis. The off-critical curves often have very notable curvature, i.e., one will see the curves for $p < p_1$ veering downward while the curves for $p > p_1$ veer upward. This enables one to obtain accurate estimates for p_1 and the critical exponents. In Fig. 1 I have plotted the local slopes for various values of p. From the plot of $\eta(t)$ it is clear that the two lower curves, corresponding to $p = 0.1781$, and 0.1782, veers downward showing that $p_1 > 0.1782$. Likevise the upper curve, $p = 0.1785$, has a pronounced upwards curvature. Though it is less evident it also seems that the curve for $p = 0.1784$ veers upwards. All in all I conclude that $p_1 = 0.1783(1)$. This estimate differs quite a bit from that of Yaldram *et al.* ($p_1 = 0.185(2)$), which is probably due to the slightly different algorithms. Note that since NO adsorption is less efficient in my algorithm one would expect my estimate for p_1 to be smaller, as is also observed in the simulations. From the intercept of the critical curves with the y-axis I estimate $\delta = 0.45(1)$, $\eta = 0.220(5)$ and $z = 1.12(1)$. These values agrees very well with those obtained from computer simulations of directed percolation in (2+1)-dimensions [28], $\delta = 0.460(6)$, $\eta = 0.214(8)$ and $z = 1.134(4)$.

From these results it seems reasonable to conclude that the CO-NO model belongs to the DP universality class. However, due to the somewhat arbitrary choice of the initial configuration employed in the time-dependent simulations it would be nice to validate this conclusion through other means. To this end I have also performed extensive steady-state simulations using a finite-size scaling analysis. Finite-size scaling, though originally developed for equilibrium systems, is also applicable to nonequilibrium second-order phase transitions as demonstrated by Aukrust *et. al.* [17]. Their method was later applied to models with infinitely many absorbing states [25, 26]. As in equilibrium second-order phase transitions one assumes that the (infinite-size) nonequilibrium system features a length scale which diverges at criticality as, $\xi(p) \propto \Delta^{-\nu_\perp}$, where $\nu_\perp$ is the correlation length exponent in the space direction. The basic finite-size scaling ansatz is that the various quantities depend on system-size only through the scaled length L/ξ, or equivalently through the variable $\Delta L^{1/\nu_\perp}$, where L is the linear extension of the system. Thus we assume that the density of empty sites (which will be used as the order parameter of the model) depends on system size and distance from the critical point as:

$$\rho_s(p, L) \propto L^{-\beta/\nu_\perp} \mathcal{F}(\Delta L^{1/\nu_\perp}), \tag{11}$$

such that at p_1

$$\rho_s(p_1, L) \propto L^{-\beta/\nu_\perp}. \tag{12}$$

In ρ_s, and other quantities, the subscript s indicates an average taken over the *surviving* samples. Fig. 2 shows a plot of the average concentration of particles $\log_2[\rho_s(p_1, L)]$ as a function of $\log_2 L$ at the critical point, $p_1 = 0.1783$. All simulations were performed on lattices of size $L \times L$ using periodic boundary conditions. The maximal number of timesteps in each trial, t_M, and number independent samples, N_S, varied from $t_M = 300$, $N_S = 50,000$ for $L = 8$ to $t_M = 125,000$, $N_S = 500$ for $L = 256$. The slope of the line drawn in the figure is $\beta/\nu_\perp = 0.81$, which comes from the DP estimate $\beta/\nu_\perp = 0.81(2)$, using the earlier cited estimate for β and $\nu_\perp = 0.729(8)$ [28]. The data falls very nicely on the line drawn using the DP estimate thus confirming that the model belongs to the DP universality class.

Near the critical point the order parameter fluctuations grow like a power law, $\chi_s = L^d(\langle \rho^2 \rangle - \langle \rho \rangle^2) \propto \Delta^\gamma$, from which we expect the following finite-size scaling form,

$$\chi_s(p, L) \propto L^{\gamma/\nu_\perp} \mathcal{G}(\Delta L^{1/\nu_\perp}), \tag{13}$$

6

such that at p_1

$$\chi_s(p_1, L) \propto L^{\gamma/\nu_\perp}. \tag{14}$$

Fig. 3 shows a plot of $\log_2[\chi_s(p_1, L)]$ vs $\log_2 L$. The slope of the straigth line is 0.39 as obtained from the DP value $\gamma/\nu_\perp = 0.39(2)$, where I used that $\gamma = \gamma^{DP} - \nu_\parallel = 0.285(11)$ with $\gamma^{DP} = 1.571(6)$ [28]. The excellent agreement between the data and the DP-expectation confirms the DP critical behaviour of this model.

One expects a characteristic time for the system, say the relaxation time, to scale like

$$\tau(p, L) \propto L^{-\nu_\parallel/\nu_\perp} \mathcal{T}(\Delta L^{1/\nu_\perp}), \tag{15}$$

such that at p_1

$$\tau(p_1, L) \propto L^{-\nu_\parallel/\nu_\perp}. \tag{16}$$

In Fig. 4 I have plotted $\log_2[\tau_h(p_1, L)]$, where τ_h is the time it takes for half the samples to enter an absorbing state, as a function of $\log_2 L$. The slope of the line drawn in the figure is $\nu_\parallel/\nu_\perp = 1.764$, as obtained from the DP estimate [28] $\nu_\parallel/\nu_\perp = 1.764(7)$. The DP estimate is derived from the scaling relation $\nu_\parallel/\nu_\perp = 2/z$ using the earlier cited estimate for z. As can be seen the data for the CO-NO model is again fully compatible with DP critical behaviour.

One may also study the dynamical behaviour by looking at the time dependence of $\rho_s(p_1, L, t)$. For $t \gg 1$ and $L \gg 1$ one can assume a scaling form

$$\rho_s(p_1, L, t) \propto L^{-\beta/\nu_\perp} \mathcal{H}(t/L^{\nu_\parallel/\nu_\perp}). \tag{17}$$

At p_1 the system shows a power law behaviour for $t < L^{\nu_\parallel/\nu_\perp}$ before finite-size effects become important. Thus for $L \gg 1$ and $t < L^{\nu_\parallel/\nu_\perp}$, $\rho(p_1, L, t) \propto t^{-\theta}$. From Eq. (17) we see that this is the case for large L only if $\theta = \beta/\nu_\parallel$. It can be shown [11] that this ratio also equals the critical exponent δ. Fig. 5 shows the short-time evolution of the concentration of empty sites at p_1 with $L = 256$, $t_M = 10,000$, and $N_S = 1000$. The asymptotic behaviour is consistent with $\theta = 0.45$, as seen from the slope of the line. This estimate agrees well with the value for directed percolation $\theta = \delta = 0.460(6)$, or the estimate $\delta = 0.45(1)$ obtained from the time-dependent simulations presented above.

In conclusion, we have provided very convincing evidence that the critical exponents of the two dimensional CO-NO model are the same as those of directed

percolation in (2+1)-dimensions. This is the first time that a two dimensional multi-component model with infinitely many absorbing states has been firmly placed in the DP universality class. This results lends further support to the extensions of the DP conjecture to models with multiple components [30] and/or infinitely many absorbing states [25, 26], at least in cases where the absorbing states can be characterized by the vanishing of a unique quantity.

References

[1] Several articles about directed percolation may be found in *Percolation Structures and Processes*, edited by G. Deutsher, R. Zallen, and J.Adler, Annals of the Israel Physical Society Vol. 5 (Hilger, Bristol, 1983).

[2] J. Blease, J. Phys. C **10**, 917, 923, and 3461 (1977).

[3] J. L. Cardy and R. L. Sugar, J. Phys. A **13**, L423 (1980).

[4] W. Kinzel, Z. Phys. B **58**, 229 (1985).

[5] V. N. Gribov, Sov. Phys. JETP **26**, 414 (1968); V. N. Gribov and A. A. Migdal, Sov. Phys. JETP **28**, 784 (1969).

[6] R. C. Brower, M. A. Furman, and M. Moshe, Phys. Lett. B **76**, 213 (1978).

[7] T. E. Harris, Ann. Prob. **2**, 969 (1974).

[8] T. M. Liggett, *Interacting Particle Systems* (Springer-Verlag, New York, 1985).

[9] R. Durrett, *Lecture Notes on Particle Systems and Percolation* (Wadsworth Pub. Co., Pacific Grove, CA, 1988).

[10] F. Schlögl, Z. Phys. B **253**, 147 (1972).

[11] P. Grassberger and A. de la Torre, Ann. Phys. (NY) **122**, 373 (1979).

[12] H. K. Janssen, Z. Phys. B **42**, 151 (1981).

[13] P. Grassberger, Z. Phys. B **47**, 365 (1982).

[14] R. M. Ziff, E. Gulari, and Y. Barshad, Phys. Rev. Lett. **56**, 2553 (1986).

[15] R. Bidaux, N. Boccara, and H. Chaté, Phys. Rev. A **39**, 3094 (1989).
I. Jensen, Phys. Rev. A **43**, 3187 (1991).

[16] R. Dickman, Phys. Rev. B **40**, 7005 (1989).

[17] T. Aukrust, D. A. Browne, and I. Webman, Phys. Rev. A **41**, 5294 (1990)

[18] R. Dickman, Phys. Rev. A **42**, 6985 (1990).

[19] R. Dickman and Tania Tomé, Phys. Rev. A **44**, 4833 (1991).

[20] H. Takayasu and A. Yu Tretyakov, Phys. Rev. Lett. **68** 3060 (1992).
I. Jensen, Phys. Rev E **47**, R1 (1993).
I. Jensen, J. Phys. A **26**, 3921 (1993).

[21] H. Park, J. Köhler, I-M Kim, D. ben-Avraham, and S. Redner, J. Phys. A **26**, 2071 (1993).

[22] J. Zhuo, S. Redner, and H. Park, J. Phys. A **26**, 4197 (1993).

[23] J. Köhler and D. ben-Avraham, J. Phys. A **24**, L621 (1991); D. ben-Avraham and J. Köhler, J. Stat. Phys. **65**, 839 (1992).

[24] E. V. Albano, J. Phys. A **25**, 2557 (1992); A. Maltz and E. V. Albano, Surf. Science **277**, 414 (1992); E. V. Albano, J. Stat. Phys. **69**, 643 (1992).

[25] I. Jensen, Phys. Rev. Lett. **70**, 1465 (1993).

[26] I. Jensen and R. Dickman, Phys. Rev. E **48**, 1710 (1993).

[27] K. Yaldram, K. M. Khan, N. Ahmed, and M. A. Kkan, J. Phys. A **26**, L801 (1993).

[28] P. Grassberger, J. Phys. A **22**, 3673 (1989).

[29] J. F. F. Mendes, R. Dickman, M. Henkel, and M. C. Marques, *Generalized Scaling for Models with Multiple Absorbing States*, preprint 1993.

[30] G. Grinstein, Z. W. Lai, and D. Browne, Phys. Rev. A **40**, 4820 (1989).

Figure Captions

Figure 1 Local slopes $-\delta(t)$ (upper panel), $\eta(t)$ (middle panel), and $z(t)$ (lower panel), as defined in Eq. 10 with $m = 5$. Each panel contains five curves with, from bottom to top, $p = 0.1781, 0.1782, 0.1783, 0.1784$ and 0.1785.

Figure 2 The concentration of empty sites $\log_2[\rho_s(p_1, L)]$ *vs* $\log_2 L$. The slope of the straight line is $\beta/\nu_\perp = 0.81$.

Figure 3 The fluctuations in the concentration of empty sites $\log_2[\chi_s(p_1, L)]$ *vs* $\log_2 L$. The slope of the straight line is $\gamma/\nu_\perp = 0.39$.

Figure 4 The time before *half* the samples enter an absorbing state $\log_2[\tau_h(p_1, L)]$ *vs* $\log_2 L$. The slope of the straight line is $\nu_\parallel/\nu_\perp = 1.764$.

Figure 5 Log-log plot of $\rho_s(p, L, t)$, for $p = p_1 = 0.1783$ and $L = 256$, as a function of t. The slope of the straight line is $\theta = 0.45$.