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On the universality classes of the discontinuous irreversible phase transitions of a multicomponent reaction system

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Abstract. Discontinuous irreversible phase transitions (IPTs) from active states to absorbing (poisoned) states in a trimolecular irreversible reaction model, which involves one monomer and two different dimers, are studied by means of Monte Carlo simulations. Evaluated dynamic critical exponents strongly suggest that each first-order IPT has its own universality class.

1. Introduction

The study of irreversible phase transitions (IPTs) in reaction systems has attracted growing attention due to their interest in many branches of science and technology: physical chemistry, biology, astrophysics, ecology, catalysis, etc. One of the major achievements in the study of these irreversible critical phenomena is the discovery that continuous IPTs belong to the same universality class, namely that of directed percolation (DP) or Reggeon field theory ([1–7], and references therein). It is known that, on the one hand, many models satisfy the DP universality class ([1–7], and references therein), but on the other hand counter-examples have been found [8–11]. In contrast to the important advance in the understanding of continuous IPTs, the study of discontinuous (first-order) IPTs is still in its infancy. For example, Evans *et al* [12, 13] have evaluated critical exponents characteristic of the first-order IPT of the ZGB model [14]. Also, we have evaluated the same exponents for various models exhibiting a single (trivial) critical point [15]. The results obtained indicated that all transitions belong to different universality classes [15].

Within this context, the aim of the present work is to determine critical exponents characteristic of the first-order IPTs of a recently proposed trimolecular (TM) model. For some particular choice of the parameters, the studied model maps into both the ZGB [14] and the dimer–dimer (DD) [16–19] models. Therefore the evaluation of their critical exponents would also allow us to gain insight into the crossover between both models.

2. Description of the model and the simulation method

The reaction model involves one monomer (A) and two dimers (B_2 and C_2), so it is a TM reaction system. The TM surface reaction schema is based upon the Langmuir–Hinshelwood

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mechanism, i.e. all reactants are adsorbed on the surface. Then, it is assumed that the reaction occurs according to the following steps:

$$A(g) + (^*) \rightarrow A(g) \tag{1a}$$

$$B_2(g) + 2(^*) \rightarrow 2B(a) \tag{1b}$$

$$C_2(g) + 2(^*) \rightarrow 2C(a) \tag{1c}$$

$$A(a) + B(a) \rightarrow AB(g) + (^*) \tag{1d}$$

$$B(a) + C(a) \rightarrow BC(a) + (^*) \tag{1e}$$

$$BC(a) + B(a) \rightarrow B_2C(g) + 2(^*) \tag{1f}$$

where (*) denotes a vacant site on the catalyst surface, while (a) and (g) refer to the adsorbed and gas phases, respectively. Equations (1*a*), (1*b*) and (1*d*) correspond to the oxidation of carbon monoxide (the ZGB model [3,4,12–14]), i.e. A $\equiv$ CO, $B_2 \equiv O_2$ and AB $\equiv CO_2$. Furthermore, equations (1*b*), (1*c*), (1*e*) and (1*f*) correspond to the oxidation of hydrogen (the DD model [16–19]), i.e. $B_2 \equiv O_2$, $C_2 \equiv H_2$ and $C_2B \equiv H_2O$, which also involves the formation of the intermediate adsorbed species BC $\equiv$ OH.

Surface sites can be empty or occupied by A, B, C and BC species. The gas phase in contact with the catalyst surface is assumed to be kept at constant pressure and composition of A, B_2 and C_2 molecules. So, the respective rate of arrival and subsequent sticking coefficients are y_A, y_B and y_C, which are normalized such that $y_A + y_B + y_C = 1$, and consequently one can use only two parameters, namely y_A and y_C. Note that for $y_C = 0$ ($y_A = 0$) one recovers the ZGB [14] (DD [16–19]) model, respectively.

The TM reaction is simulated on the homogeneous square lattice of side $L = 200$ using periodic boundary conditions. The simulation algorithm may be briefly summarized as follows. (i) A site (say site 1) of the surface is selected at random. (ii) If the site is occupied the trial ends. Otherwise, if the site is empty a molecule of type A, C_2 or B_2 is selected at random with probabilities y_A, y_C and $y_B = 1 - y_C - y_A$, respectively. (iii) If the selected species is a monomer, it is adsorbed on the site and the corresponding four nearest-neighbour (NN) sites are checked for the presence of B(a) in order to satisfy equation (1*d*). (iv) If the selected species is a dimer then one has to select at random a NN site (say site 2). If site 2 is occupied the trial ends because there is no place for dimer adsorption. Otherwise, the dimer is adsorbed and the corresponding six NN sites are checked for the presence of A(a), B(a), C(a) and BC(a) in order to satisfy equations (1*d*)–(1*f*). A random decision is taken when more than one reaction path is possible. After reaction the products are removed from the surface. Further details on the simulation algorithm follow from the description of both the ZGB [3, 4, 12–14] and the DD [16–18] models.

The Monte Carlo time unit is defined such that each site of the surface is visited once, on average.

3. Results and discussion

3.1. The phase diagram of the TM model

Taking $y_C = 0$ the TM model is mapped onto the ZGB model [14]. That is, for $y_{1A} \leqslant 0.3905$ ($y_{2A} \geqslant 0.525$) the surface becomes fully covered by B (A) species, respectively. That

is, the system becomes irreversibly poisoned by the reactants and the production of AB stops. These poisoned states are unique in the sense that they correspond to a single configuration of the covered surface. Within the interval $y_{1A} < y_A < y_{2A}$ one observes sustained production of AB, and therefore both y_{1A} and y_{2A} are critical points at which irreversible phase transitions between the reactive regime and poisoned states of the surface take place. The transition at y_{1A} is continuous (second order) while the transition at y_{2A} is discontinuous (first order). The ZGB model corresponds to the horizontal axis in figures 1(*a*) and 1(*b*); for additional details see [14].

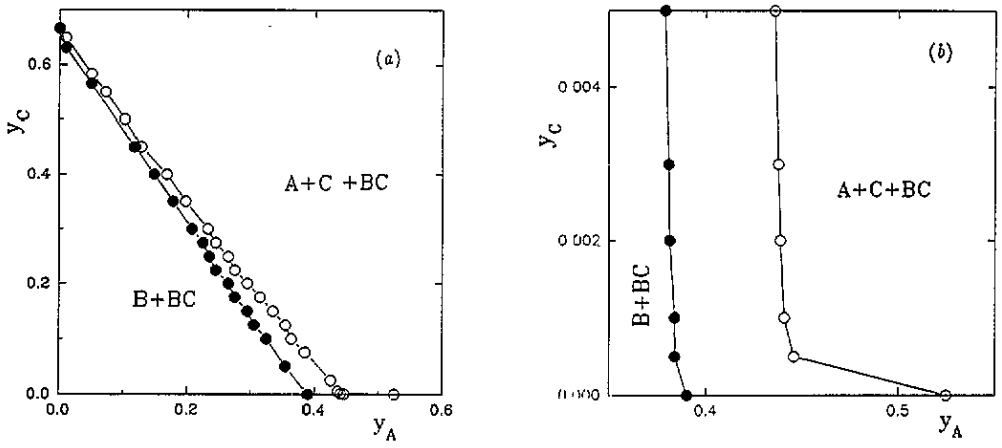

Figure 1. (*a*) Plot of the critical points y_C versus y_A of the TM model: ●, second-order IPTs; ○, first-order IPTs. (*b*) Detailed view of (*a*) in the $y_C \to 0$ limit.

On the other hand, taking $y_A = 0$ the TM model is mapped onto one variant of the DD model termed M1 in reference [17]. Now one has a single critical point at $y_{1C} = \frac{2}{3}$ such that for $y_C < y_{1C}$ ($y_C > y_{1C}$) the surface becomes poisoned by a binary compound of {B + BC} species (B-species), respectively. The transition at y_{1C} is of first order. Note that in this case the poisoned states are non-unique. In fact, on the one hand, one has an infinity of possibilities to construct the binary compound; for a detailed discussion on the nature of the binary compound see [16–18]. On the other hand, since the TM model neglects the diffusion of the reactants the poisoned state with B-species is jammed, i.e. a unitary coverage cannot be achieved due to spatial restrictions for dimer adsorption [17], so one has again infinite different poisoned states. The DD model corresponds to the vertical axis of figure 1(*a*); for additional details see [16–19].

Taking both $y_A > 0$ and $y_C > 0$ one can construct the complete phase diagram of the TM model, as shown in figure 1(*a*). The solid circles in figures 1(*a*) and 1(*b*) indicate second-order IPTs from poisoned states with binary compounds of {B + BC} species and the reactive regime with production of both AB and C_2B species. The surface coverage with B and BC species within the poisoned states depends on both y_A and y_C, and these states are non-unique. Open circles in figures 1(*a*) and 1(*b*) show first-order IPTs from the reactive regime to poisoned states with {A + B + AB} species. Again, these states are non-unique and the concentration of the species also depends on both y_A and y_C. From figure 1(*a*) it follows that in the presence of traces of C ($y_C \to 0$) the first-order IPT characteristic of the ZGB model ($y_C = 0$) becomes drastically shifted towards lower y_A values. In fact, it seems that several open circles may lie along the $y_C = 0$ line. This behaviour can better

be understood after inspection of the figure 1(*b*), which shows the phase diagram of the TM model in the limit $y_C \to 0$. On the other hand, in the limit $y_A \to 0$ the first-order and second-order transitions are very close, collapsing in a single critical point just at $y_A = 0$. For $y_A > 0$ the thin intermediate region between the two phase boundaries corresponds to the reactive state with production of both AB and C_2B species. Of course, the amount of C_2B (AB) increases (decreases) when approaching the limiting value $y_A = 0$. Just at $y_A = 0$ one has only C_2B production during a transient period because it is believed [16–18] that in the $t \to \infty$ limit (and even for $L = \infty$) the final state of the lattice will be a poisoned one with either the binary compound or B-species.

The critical points of the phase diagram of figures 1(*a*) and 1(*b*) are determined by studying the poisoning dynamics as described below. Further details on the phase diagram of the TM model have already been published [20].

3.2. *Evaluation of dynamic critical exponents at the discontinuous IPTs*

It has been established that a fruitful approach to gain insight on the universality class of IPTs is to calculate exponents related to the time-dependent critical behaviour of the process [4–8, 10, 12, 13, 15]. For this purpose one proceeds as follows. Simulations start with lattices completely poisoned except for a blob of empty sites at the centre of the sample. Then, the time evolution of the blob embedded in the poisoned state is monitored. The measured quantities are: (i) the survival probability $P(t)$, that is, the probability that the sample was not poisoned after t time steps; and (ii) the average number of empty sites $N(t)$. Averages are taken over K independent realizations (or runs). Each run proceeds until some fixed maximum time t_M, unless the sample becomes poisoned before t_M. At the critical point and in the $t \to \infty$ limit it is expected that the following scaling laws should hold:

$$P(t) \propto t^{-\delta} \tag{2}$$

and

$$N(t) \propto t^{\eta}. \tag{3}$$

So, the asymptotic slopes of log–log graphs of equations (2) and (3) define the dynamic critical exponents δ, and η, respectively. Let us note that working with a unique absorbing state the construction of the starting (poisoned) configuration is straightforward. Nevertheless, in the case of non-unique absorbing states the initial configuration to be used in time-dependent simulations has to be generated running the system within the poisoned phase but close to critically, in order to have not only the proper particle coverage but also to allow the system to build up the correct correlations on its own [6, 15].

Figures 2(*a*) and 2(*b*) show log–log plots of $P(t)$ and $N(t)$ verses t obtained assuming $y_C = 0.10$ and scanning y_A close to the critical value. For $y_A = 0.355$ ($y_A = 0.365$) one has that $N(t)$ veers downwards (upwards) in the limit $t \to 10^3$, suggesting that these y_A values are slightly off critically. In contrast, for $y_A = 0.360$ a power law decay is observed according to equation (3). A similar behaviour is observed for the curve $P(t)$ versus t (figure 2(*a*)). Using this procedure we determine the critical point at $y_C = 0.10$ and $y_A \cong 0.360 \pm 0.005$, and the corresponding critical exponents are listed in table 1.

In order to study the critical behaviour of the TM model, critical exponents are also calculated at different critical points (see figures 3 and 4). Figures 3(*a*) and 3(*b*) have been obtained taking $y_C = 0.30$ and scanning y_A. The critical point is close to $y_A \cong 0.2250 \pm 0.0025$, since $y_A = 0.2275$ is clearly off critically as follows from the

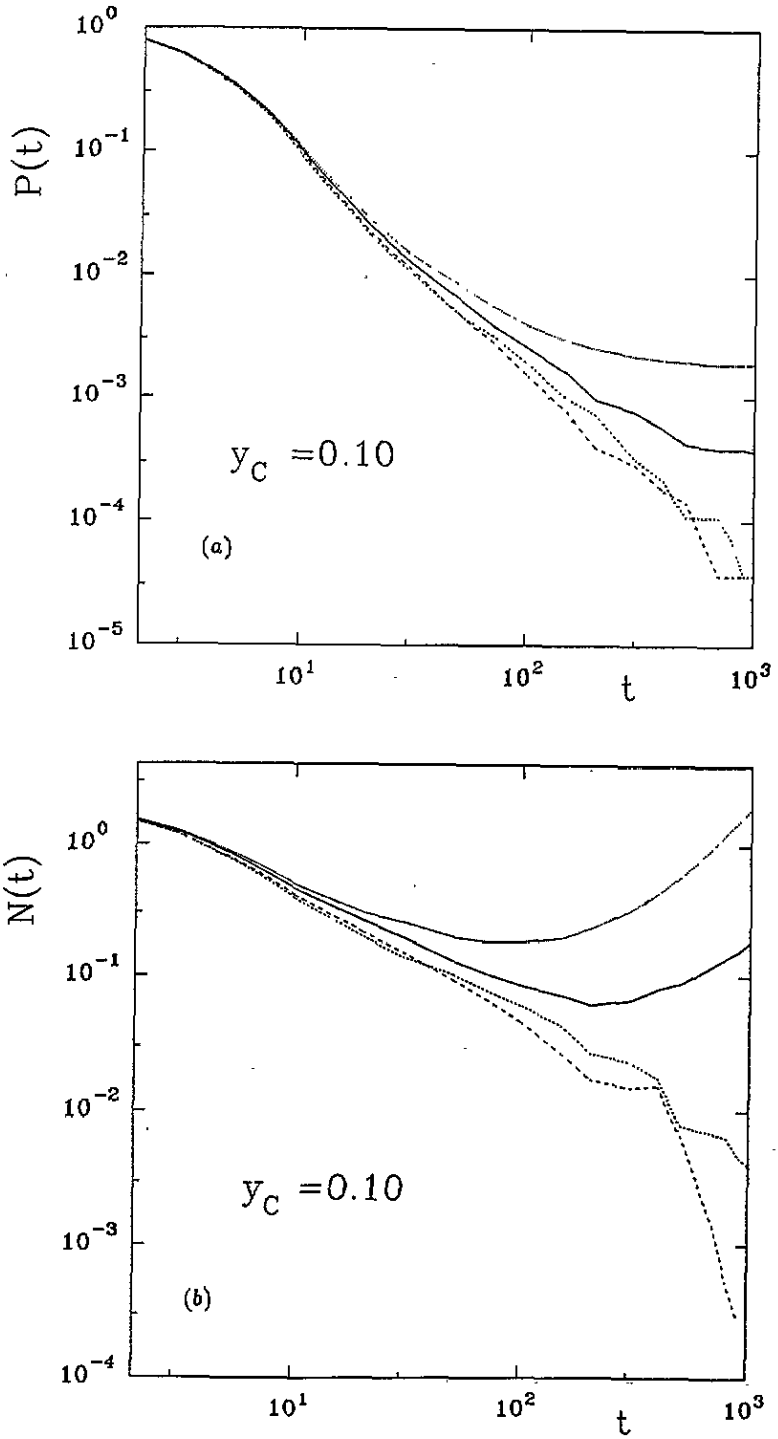

Figure 2. Log–log plots of (*a*) $P(t)$ and (*b*) $N(t)$ versus t, respectively. Results obtained for $y_C = 0.10$ and different choices of y_A are, from bottom to top: $y_A = 0.355$, 0.360, 0.365 and 0.370. Averages are taken over $K = 5 \times 10^4$ independent runs up to $t_M = 10^3$. Critical exponents listed in table 1 are obtained fitting the asymptotic regime of the curve corresponding to $y_A = 0.360$. For further details, see the main text.

Table 1. List of critical points (y_A, y_C) and the corresponding dynamic critical exponents for the TM model discussed in the text. The quoted error ranges merely reflect the statistical error.

y_A	y_C	δ	η	Reference
0.00	2/3	0.920 ± 0.001	-0.25 ± 0.03	[15]
0.05	0.5763	3.377 ± 0.134	-1.750 ± 0.053	PW
0.2250	0.30	2.782 ± 0.054	-1.756 ± 0.035	PW
0.3600	0.10	1.533 ± 0.040	-0.926 ± 0.044	PW
0.525	0.0	3.70	-2.20	[12, 13]
0.3905	0.0	0.452 ± 0.008	0.224 ± 0.01	[4]

PW, present work.

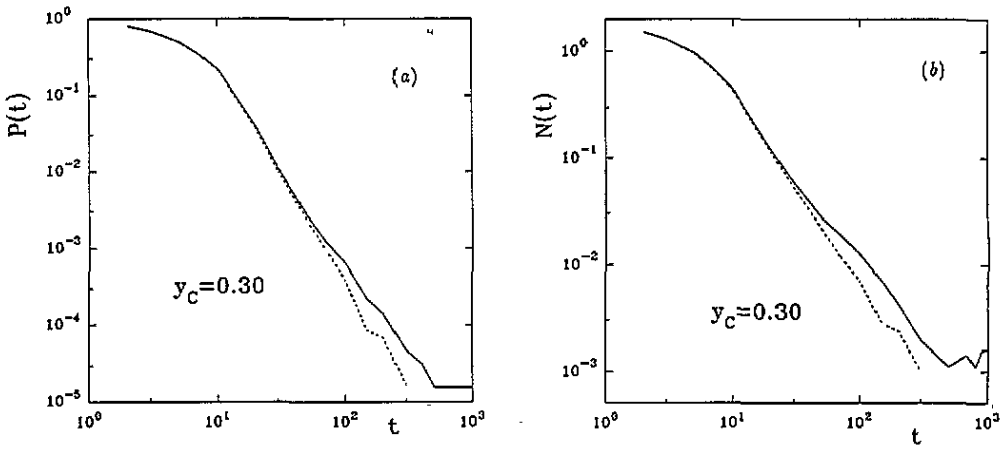

Figure 3. Log–log plots of (*a*) Pt and (*b*) $N(t)$ versus t, respectively. Results obtained for $y_C = 0.30$ and two different choices of y_A are, from bottom to top: $y_A = 0.225$ and 0.2275. Averages are taken over $K = 5 \times 10^4$ independent runs up to $t_M = 10^3$. Critical exponents listed in table 1 are obtained fitting the asymptotic regime of the curve corresponding to $y_A = 0.225$. For further details, see the main text.

figures. The obtained critical exponents are listed in table 1. A similar study has been performed at $y_A = 0.05$ and scanning y_C (figures 4(*a*) and 4(*b*)). The obtained results are also listed in table 1.

For the sake of comparison, table 1 also contains the critical exponents of both the DD model ($y_A = 0$ and $y_C = \frac{2}{3}$) [15] and the ZGB model ($y_A \cong 0.525$ and $y_C = 0$) [12, 13]. The exponents characteristic of the continuous IPT of the ZGB model ($y_A \cong 0.3905$ and $y_C = 0$) [4] are are also listed in table 1. These exponents correspond to the DP universality class.

Due to the lack of a satisfactory theory capable of describing first-order irreversible phase transitions in reaction systems the explanation of the obtained results on the basis of analytical arguments is not possible. However, the physical picture behind the performed epidemic analysis can be understood in terms of the description outlined by Evans *et al* [12]. Our epidemic analysis reveals that, within the reactive regime but even very close to the critical point, most of the initially empty blobs embedded in the poisoned state becomes quickly poisoned (e.g. see figure 2(*a*)). However, later on, a few surviving epidemic blobs eventually prevail, spreading the reactive steady state across the entire sample (e.g. see figure 2(*b*)). The large positive δ-values and the large *negative* η-values (see table 1) reveal a greatly reduced epidemic survivability. In contrast, the conventional epidemic behaviour

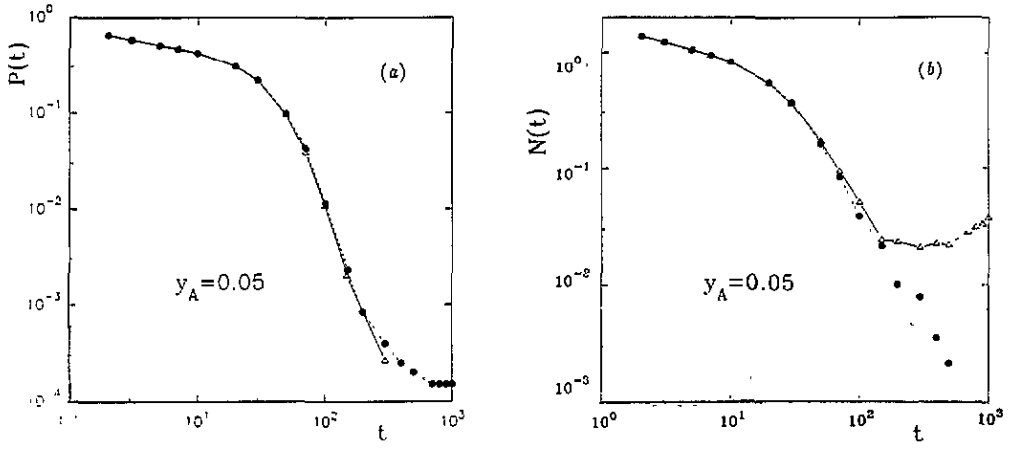

Figure 4. Log–log plots of (*a*) $P(t)$ and (*b*) $N(t)$ versus t, respectively. Results obtained for $y_A = 0.05$ and different choices of y_C are, from bottom to top: $y_C = 0.5763$ and 0.5775. Averages are taken over $K = 5 \times 10^4$ independent runs up to $t_M = 10^3$. Critical exponents listed in table 1 are obtained fitting the asymptotic regime of the curve corresponding to $y_C = 0.5763$. *For further details, see the main text.*

characteristic of DP-type continuous transitions produce small positive values for δ and η (see table 1).

After inspection of the exponents listed in table 1 it also follows that *all* discontinuous IPTs have different critical exponents, indicating that each transition has its own universality class. Furthermore, the crossover of the critical exponents, from the ZGB to the DD model, does not follow a monotonic behaviour. These results point out that the theoretical description of discontinuous IPTs has to be much more complex than that of continuous IPTs. The fact that the poisoned states are non-unique (except for $y_C = 0$) and that the concentrations of poisoning species are different at each IPT may play a relevant role in the case of discontinuous IPTs since the concentration of these species may have a considerable effect on the survival probability of the empty blobs and the subsequent epidemic spreading of the reactive regime. In contrast, it has been found very recently that continuous IPTs in non-unique poisoned states also belong to the DP universality class. This statement holds for both single component and multicomponent reaction systems, e.g. as in [6] and [7], respectively.

4. Conclusions

Dynamic critical exponents of first-order irreversible phase transitions of a TM reaction model have been evaluated. Since all transitions have different exponents it follows that each transition has its own universality class. This behaviour is in contrast to the second-order transitions which belong to the DP universality class [7]. These results indicate that the critical behaviour of discontinuous transitions is far more complex than that of continuous transitions and therefore deserves further studies.

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