

On the influence of the hot dimer adsorption mechanism in the critical behaviour of the ZGB model

This article has been downloaded from IOPscience. Please scroll down to see the full text article.

1994 J. Phys. A: Math. Gen. 27 7763

(<http://iopscience.iop.org/0305-4470/27/23/019>)

View [the table of contents for this issue](#), or go to the [journal homepage](#) for more

Download details:

IP Address: 171.66.16.68

The article was downloaded on 01/06/2010 at 22:47

Please note that [terms and conditions apply](#).

On the influence of the hot dimer adsorption mechanism in the critical behaviour of the ZGB model

Ezequiel V Albano† and Victor D Pereyra‡§

† Inifta-Universidad Nacional de La Plata, CC 16, Suc. 4 (1900) La Plata, Argentina

‡ Institut für Physik, Johannes Gutenberg Universität Mainz Postfach 3980, Staudinger Weg 7, W-6500 Mainz, Germany

Received 23 December 1993, in final form 5 July 1994

Abstract. Hot dimers are molecules that dissociate after adsorption and the resulting monomers undergo a ballistic flight up to a distance R from the adsorption site. The influence of this adsorption mechanism on the critical behaviour of the ZGB model for the catalysed reaction $\text{CO} + \frac{1}{2}\text{O}_2(\text{Hot}) \rightarrow \text{CO}_2$ is studied by means of Monte Carlo simulations. It is found that the critical thresholds at which second and first-order irreversible phase transitions (IPTs) take place depend on R . The universality class of the second-order IPT is independent of R , e.g. the evaluated critical exponents are the same than those of the standard ZGB model with $R = 0$. However, critical exponents characteristic of the first-order IPT can be tuned varying R , indicating non-universal behaviour. The evolution of empty surface patches in a sea of CO-species, close to the first-order IPT, can be understood in terms of an epidemic oxidation growth.

1. Introduction

Heterogeneously catalysed reactions frequently deal with complex mechanisms consisting of a vast number of elementary processes. Since the handling of such a large number of mechanisms imposes severe problems, the usual procedure is to rationalize the study by analysing such elementary steps separately [1, 2]. Within this context the catalytic oxidation of carbon monoxide has been extensively studied [2–29]. It has been established that this reaction follows the Langmuir–Hinshelwood mechanism [3]:



Here $*$ represent a vacant site on the catalyst surface and (g) and (ad) denote the gas and adsorbed phase, respectively.

Several models have been proposed for describing the reaction given by equations (1)–(3) [2–29] (and references therein). However, recently a simple model proposed by Ziff, Gulari and Barshad [6] (the ZGB model) has received considerable attention [6, 7, 9, 13–29]. The ZGB model uses a square lattice to represent the catalytic surface. CO and O₂ molecules are selected randomly with relative probabilities Y and $(1 - Y)$, respectively, and an attempt

§ Permanent address: Departamento de Física-Universidad Nacional de San Luis, Chacabuco y Pedernera (5700) San Luis, Argentina.

is made to add the selected species to the surface. If the selected species is CO, one surface site is selected at random, and if that site is vacant, the CO is adsorbed on it (equation (1)). Otherwise, if that site is occupied, the trial ends and a new molecule is selected. If the selected species is O₂, a pair of nearest neighbour (NN) sites are selected at random and the molecule is added to them only if they are both vacant (equation (2)). After each adsorption event, the NN sites of the added molecule are examined in order to account for the reaction given by equation (3). If more than one {O(ad), CO(ad)} pair formed as a consequence of the newly adsorbed species is identified, a single one is selected at random and removed from the surface.

Interest in the ZGB model arises due to rich and complex irreversible critical behaviour. In fact, in the asymptotic regime, $t \rightarrow \infty$, the system reaches a stationary state whose nature solely depends on the parameter Y . For $Y \leq Y_{1c} \cong 0.3907$ ($Y \geq Y_{2c} \cong 0.525$) the surface becomes irreversibly poisoned by O (CO)-species, while for $Y_{1c} < Y < Y_{2c}$ a steady state with sustained production of CO₂ is observed [6]. So, just at Y_{1c} and Y_{2c} the model exhibits irreversible or kinetic phase transitions (IPTs) between the reactive regime and poisoned states which are of second and first order, respectively.

Since the ZGB model is a simplified description of the actual catalytic reaction, a number of studies have been performed in order to investigate the influence of relevant additional parameters such as, for example, diffusion and desorption of the reactants [9, 13, 15, 19, 21, 24, 28], lateral interactions between the adsorbed species [13, 23, 27], the sticking coefficient of the incoming molecules [12, 29], the finite size and the fractal nature of the underlying substratum [14, 16, 18, 21, 25, 26], the addition of an Eley-Rideal reaction step [17, 20], etc.

Within this context, the aim of the present work is to investigate the influence of the hot dimer adsorption mechanism on the critical behaviour of the ZGB model. Hot dimers are molecules that dissociate upon chemisorption and the resulting monomers undergo a ballistic flight up to distance R from the original adsorption site. This study is also motivated by the fact that in previous simulations we have found that monomers resulting from hot dimer dissociation have enhanced the probability for encounters with adsorbed atoms [30] and consequently the catalytic activity of these species becomes enlarged [31].

The hot dimer adsorption mechanism have very recently been observed by Brune *et al* [32, 33] using scanning tunnelling microscopy measurements. In fact, it has been demonstrated that oxygen molecules chemisorb dissociatively on the Al(111) surface and that at least part of their excess energy shows up in degrees of freedom parallel to the surface, giving rise to translational motion during which this energy is dissipated. Evidences are given in order to show that this 'hot' species flies apart, on the average, by at least $R \cong 40 \text{ \AA}$ before being immobile adsorbed. Note that the transient mobility caused by the inability to instantaneously dissipate the energy gained by a particle after formation of the surface bond seems to be a common process in nature. In fact, surface hopping of hot adatoms resulting from dimer dissociation has been considered in models for the chemisorption of nitrogen on the (100) face of tungsten [34, 35]. Also, the influence of the hot dimer adsorption mechanism on the catalysed reaction $\text{H}_2(\text{hot}) + \frac{1}{2}\text{O}_2 \rightarrow \text{H}_2\text{O}$ on polycrystalline Pt, has been analysed by means of a mean field approach in the early works of Harris *et al* [36]. Furthermore, the formation of metastable ordered structures upon oxygen adsorption on Pd(100) [37, 38 and references therein] has also been understood assuming hot O₂-dissociation, where probably the distance travelled by the monomers is rather short, namely a few lattice units. Very recently, evidence has been reported on the hot-monomer adsorption mechanism [39].

The paper is organized as follows: in section 2 a brief description of the method used to

simulate the adsorption–reaction process is given. In section 3 the theoretical background and the method employed to obtain critical thresholds and critical exponents related to the time-dependent critical behaviour of the model are described. In section 4 we present our results, focusing the discussion on the universality class of the model. Finally, our conclusions are stated in section 5.

2. Brief description of the adsorption–reaction scheme

The reaction is simulated on the homogeneous square lattice of side $L = 200$ using periodic boundary conditions. The reaction scheme of the ZGB model has been outlined in the introduction. Further details can be found in a number of publications [6, 7, 9, 13–29]. In order to account for the hot dimer adsorption mechanism the following modifications have to be introduced: after adsorption of one dimer the six NN sites of the added molecules are examined in order to account for the reaction given by equation (3). If at least one oxygen atom has not reacted, the hot adsorption mechanism begins to operate. The oxygen atom undergoes a ballistic flight up to a maximum distance R measured from the initial adsorption site. Note that Y and R are the only parameters of the model. The flight is assumed to be parallel to the axis of the ‘hot’ dimer upon adsorption. During the flight all NN sites to the trajectory are examined for the presence of CO(ad) and if this species is detected the reaction given by equation (3) is assumed to take place. Otherwise, if the flying oxygen atom hits another oxygen which is already at rest, the flying monomer is frozen on the NN site adjacent to the adsorbed oxygen in the direction of the flight.

In the simulations we have restricted ourselves to work within the range $0 \leq R \leq 20$ (R measured in lattice units), taking into account the experimental value $R \cong 40 \text{ \AA}$ [32, 33], i.e. equivalent to approximately 20 lattice spaces.

The Monte Carlo time unit is defined so that each site of the surface is visited once, on average. Simulations are performed in a multitransputer system with 12 T805 processors working in parallel. The codes are written in OCCAM 2, including a reliable random number generator which has been developed and tested by Paul *et al* [40].

3. The time-dependent critical behaviour

The determination of ‘static’ exponents in irreversible reaction systems, such as the order parameter critical exponent, the correlation length exponent, the susceptibility exponent, etc, is quite difficult and rather inaccurate due to finite size effects and metastabilities of the system. In fact, for $t \rightarrow \infty$ the final state of all finite system must be a poisoned one. It has been established that a fruitful approach to overcome this shortcoming is to calculate exponents related to the time-dependent critical behaviour of the process [22, 41–46]. For this purpose one proceeds as follows: simulations start with lattices completely poisoned except for a line with D empty sites placed close to the centre of the sample, so D is the length of the central hole measured in lattice units. Then, the time evolution of the hole 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; (ii) the average number of empty sites $N(t)$; and (iii) the average mean-square distance, $R^2(t)$, over which the empty sites have spread. The number of empty sites $N(t)$ is averaged over all samples, including those that have already been poisoned, while $R^2(t)$ is averaged over the runs in which the sample is not poisoned at time 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 $t \rightarrow \infty$ limit, it is expected that the following scaling laws should hold:

$$P(t) \propto t^{-\delta} \quad (4)$$

$$N(t) \propto t^\eta \quad (5)$$

and

$$R^2(t) \propto t^z. \quad (6)$$

So, just at criticality, the asymptotic slopes of log-log graphs of equations (4)–(6) define the dynamic critical exponents δ , η and z , respectively, while slightly off-criticality deviations from the asymptotic linear behaviour are expected to occur. The later property allows a precise determination of the critical threshold.

4. Results and discussion

4.1. Second-order IPTs

The standard ZGB model ($R = 0$) exhibits a second-order IPT, at $Y_{1c} \cong 0.3907$ [6,41], between a poisoned state with O-atoms to a reactive regime with sustained production of CO_2 . It has been established that this transition belongs to the universality class of directed percolation (DP), or equivalently to Reggeon field theory [42], e.g. see the dynamic critical exponents listed in table 1.

Table 1. List of critical exponents δ , η and z , defined according to equations (4)–(6). DP \equiv directed percolation in 2+1 dimensions and pw \equiv present work. Error bars corresponding to the pw merely reflect the statistical error.

| y_{1c} | R | D | δ | η | z | Reference |
|----------|-----|-----|-------------------|-------------------|-------------------|-----------|
| DP | — | — | 0.460 ± 0.006 | 0.214 ± 0.008 | 1.134 ± 0.004 | [47] |
| 0.3907 | 0 | — | 0.452 ± 0.008 | 0.224 ± 0.010 | 1.139 ± 0.005 | [42] |
| 0.4270 | 2 | 10 | 0.448 ± 0.007 | 0.221 ± 0.010 | 1.070 ± 0.006 | pw |
| 0.4365 | 20 | 2 | 0.452 ± 0.007 | 0.206 ± 0.010 | 1.096 ± 0.005 | pw |
| 0.4365 | 20 | 10 | 0.445 ± 0.007 | 0.206 ± 0.010 | 1.080 ± 0.005 | pw |

Figure 1(a), (b) and (c) show log-log plots of $N(t)$, $P(t)$ and $R^2(t)$ versus t obtained for $R = 20$ and $D = 2$ and $D = 10$. For this R -value the critical point is given by $Y_{1c}(R) \cong 0.4365 \pm 0.0005$ independent of D . The error bars in the critical points follow from the observation of upward and downward deviations of the asymptotic linear behaviour of $N(t)$ versus t which occur slightly off-criticality. In all cases the asymptotic regime is reached at earlier times for the smaller D -value but the critical exponents obtained are independent of D as is shown in table 1. The error bars quoted for the exponents merely reflect the statistical error, so possible corrections to scaling are neglected. Also, due to the epidemic method employed in the evaluation of the exponents, they are not affected by

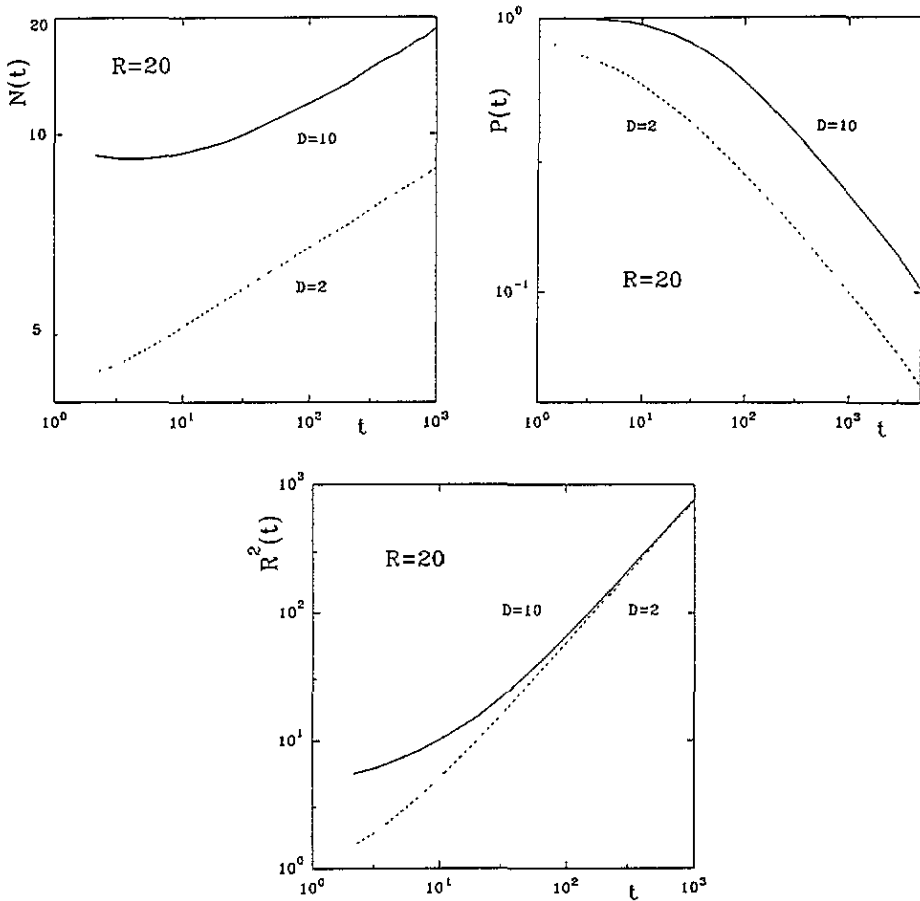


Figure 1. Log-log plots of (a) $N(t)$, (b) $P(t)$ and (c) $R^2(t)$ versus t . Results obtained for $y = 0.4365$, $R = 20$ and using holes of two different length as indicated in the figures. Averages are taken over $K = 7 \times 10^4$ independent runs up to $t_M = 10^3$. Critical exponents listed in table 1 were obtained by fitting the asymptotic regimes shown in the figures by straight lines.

finite size effects. For $R = 2$ the critical threshold is found at $Y_{1c}(R) \cong 0.427 \pm 0.001$ and the corresponding critical exponents are also listed in table 1.

The results obtained show that the hot dimer adsorption mechanism causes the critical threshold to shift toward greater Y -values when R is increased. However, as follows from the comparison of the critical exponents, the universality class of the transition does not depend on R . This finding is in agreement with the DP-conjecture, that is models with a scalar order parameter undergoing irreversible continuous transitions to a unique absorbing state (i.e. the poisoned state with O-atoms), would generically belong to the universality class of DP [42, 48–50 and references therein].

4.2. First-order IPTs

The dynamic critical behaviour of the first-order IPT of the standard ZGB model ($R = 0$), close to $Y_{2c} \cong 0.525$ [6, 22] has been studied by Evans *et al* [22]. The reported critical exponents (see table 2) clearly show that this transition does not belong to the DP universality class, as expected since it is discontinuous.

Table 2. List of critical exponents δ and η defined according to equations (4) and (5). PW \equiv present work. Error bars corresponding to the PW merely reflect the statistical error.

| y_{2c} | R | D | δ | η | References |
|----------|-----|-----|-----------------|------------------|------------|
| 0.525 | 0 | — | 3.7 ± 0.2 | -2.4 ± 0.2 | [22] |
| 0.525 | 0 | — | 3.20 ± 0.09 | -2.35 ± 0.11 | PW |
| 0.550 | 1 | 2 | 3.41 ± 0.06 | -2.41 ± 0.08 | PW |
| 0.571 | 4 | 2 | 4.62 ± 0.15 | -2.82 ± 0.10 | PW |
| 0.589 | 12 | 6 | 6.42 ± 0.11 | -5.03 ± 0.26 | PW |
| 0.595 | 20 | 10 | 7.00 ± 0.30 | -5.91 ± 0.20 | PW |

Figure 2(a) and (b) show log-log plots of $N(t)$ and $P(t)$ versus t obtained for $R = 1$ and for $D = 2$. For this R -value the first-order IPT take place close to $Y_{2c}(R) \cong 0.550 \pm 0.001$. The corresponding critical exponents are listed in table 2 together with results obtained taking other R -values. The simultaneous shift of both Y_{1c} and Y_{2c} toward higher values when R increases causes a slight enlargement of the reaction window, e.g. $\Delta = Y_{2c} - Y_{1c} \cong 0.134$ ($\Delta \cong 0.159$) for $R = 0$ ($R = 20$), respectively.

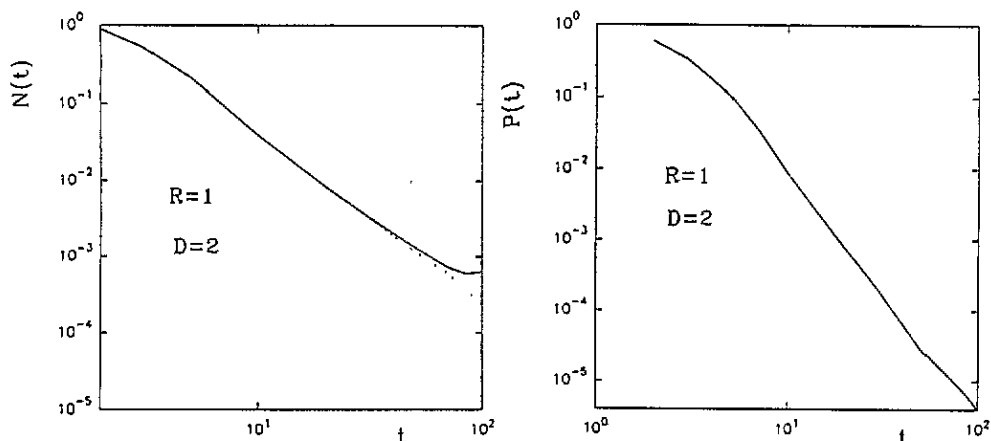


Figure 2. Log-log plots of (a) $N(t)$ and (b) $P(t)$ versus t . Results obtained for $y = 0.550$, $R = 1$ and $D = 2$. The solid curve in figure 1(a) was taken for $y = 0.549$, i.e. slightly off-criticality. Averages are taken over $K = 5 \times 10^6$ independent runs up to $t_M = 10^2$. Critical exponents listed in table 2 were obtained by fitting the asymptotic regimes shown in the figures by straight lines.

It is interesting to note that critical exponent values can be tuned varying the parameter R (see table 2). In fact, there are only a few examples of models describing standard critical phenomena where the exponents vary continuously with a parameter (see, for example, the 'butterfly model' [51], the Fisher-Ma-Nickel model [52], Lévy flights with bounded long-range hoppings in one dimension [53], etc.). In other cases where such continuously varying exponents have been reported more careful work has revealed a crossover behaviour. However, this experience gained in the study of standard critical phenomena appears to be challenged by recent results emerging from the study of irreversible critical phenomena. In fact, Evans *et al* [22] have found that the dynamic exponents δ and η corresponding to the first-order IPT of the standard ZGB model can also be tuned when the rate of reaction varies. More recently, a numerical study has shown that a monomer-dimer-dimer reaction

model exhibits first-order IPTs and that the exponents δ and η can also be tuned varying the partial pressure of the reactants [54]. The observed behaviour in [22] and [54] as well as in the present work seems to be characteristic of first-order IPTs. In spite of the fact that it cannot yet be described on the basis of solid theoretical arguments, it can be understood, at least qualitatively, in terms of oxidation epidemic growth as in the standard ZGB model [22]. In fact, near the CO-poisoned state most of the isolated empty patches quickly become CO-poisoned. However, for longer times, a few surviving oxidation centres may prevail, eventually spreading the reactive regime across the entire sample.

5. Conclusions

The influence of the hot dimer adsorption mechanism on the critical behaviour of the ZGB model is investigated. The critical threshold of the second-order IPT depends on R , but the evaluated critical exponents indicate that the universality class of the transition remains unchanged, i.e. that of directed percolation. The location of the first-order IPT also depends on R . However, critical exponents can be tuned varying R , i.e. the universality class depends on R . The obtained exponents are consistent with an oxidation epidemic or spreading process. We expect that this interesting behaviour would stimulate further work in order to achieve a theoretical understanding of the problem.

Acknowledgments

This work was supported by the Consejo Nacional de Investigaciones Científicas y Técnicas (CONICET) de la República Argentina. The Alexander von Humboldt Foundation (Germany) and Fundación Antorchas (Argentina) are greatly acknowledged for the provision of valuable equipment.

References

- [1] Engel T and Ertl G 1979 *Adv. Catal.* **28** 1
- [2] Madey T E, Yates J T Jr, Sandstrom D R and Voorhoeve R J H 1976 *Catalysis by Solid Surfaces, Treatise on Solid State Chemistry (Surfaces II)* vol 6B, ed N B Hannay (New York: Plenum) p 1
- [3] Warnatz J 1981 *Chemistry of Stationary and Non-Stationary Combustion (Springer Series in Chemical Physics 18: Modeling of Chemical Reaction Systems)* ed K H Ebert et al (Berlin: Springer) p 162
- [4] Engel T and Ertl G 1978 *J. Chem. Phys.* **69** 1267
- [5] Stuve E, Madix R and Brundle C 1984 *Surf. Sci.* **146** 155
- [6] Mukesh D, Morton W, Kenney C N and Cutlip M B 1984 *Surf. Sci.* **138** 237
- [7] Ziff R, Gulari E and Barshad Y 1986 *Phys. Rev. Lett.* **56** 2553
- [8] Meakin P and Scalapino D J 1987 *J. Chem. Phys.* **87** 731
- [9] Graham W R C and Lynch D T 1987 *Surf. Sci.* **187** L633
- [10] Fischer P and Titulaer U M 1989 *Surf. Sci.* **221** 409
- [11] Ehsasi M, Seidel C, Ruppender H, Drachsel W, Block J H and Christmann K 1989 *Surf. Sci.* **210** L198
- [12] Ehsasi M, Matloch M, Frank O, Block J H, Christmann K, Rys F S and Hirschwald W 1989 *J. Chem. Phys.* **91** 4949
- [13] Khan M A and Yaldram K 1989 *Surf. Sci.* **219** 445
- [14] Kaukonen H P and Nieminen R M 1989 *J. Chem. Phys.* **91** 4380
- [15] Albano E V 1990 *Surf. Sci.* **235** 351
- [16] Mai J, von Niessen W and Blumen A 1990 *J. Chem. Phys.* **93** 3685
- [17] Albano E V 1990 *J. Phys. A: Math. Gen.* **23** L545
- [18] Meakin P 1990 *J. Chem. Phys.* **93** 2903

- [18] Albano E V 1990 *Phys. Rev. B* **42** 10 818
- [19] Jensen I and Fogedby H C 1990 *Phys. Rev. A* **42** 1969
- [20] Mai J and von Niessen W 1991 *Chem. Phys.* **156** 63
- [21] Albano E V 1991 *J. Chem. Phys.* **94** 1499
- [22] Evans J W and Miesch M S 1991 *Surf. Sci.* **245** 401
- [23] Satulovsky J and Albano E V 1992 *J. Chem. Phys.* **97** 9440
- [24] Albano E V 1992 *Appl. Phys. A* **55** 226
- [25] Mai J, Casties A and von Niessen W 1992 *Chem. Phys. Lett.* **196** 358
- [26] Albano E V 1992 *Phys. Lett. A* **168** 55
- [27] Luque J J, Jiménez-Morales F and Lemos M C 1992 *J. Chem. Phys.* **96** 8535
- [28] Brosilow B and Ziff R 1992 *Phys. Rev. A* **46** 4534
- [29] Yaldram K, Ahmed N and Khan M A 1992 *Surf. Sci.* **274** L515
- [30] Albano E V and Pereyra V D 1993 *J. Chem. Phys.* **98** 10 044
- [31] Pereyra V D and Albano E V 1993 *Appl. Phys. A* **57** 291
- [32] Brune H, Wintterlin J, Behm R J and Ertl G 1992 *Phys. Rev. Lett.* **68** 624
- [33] Brune H, Wintterlin J, Trost J, Ertl G, Wiechers J and Behm R J 1993 *J. Chem. Phys.* **99** 2128
- [34] King D A and Wells M G 1974 *Proc. R. Soc. A* **339** 245
- [35] Wolf N O, Burgess D R and Hoffman D K 1980 *Surf. Sci.* **100** 453
- [36] Harris J and Kasemo B 1981 *Surf. Sci.* **105** L281
- Harris J, Kasemo B and Törnqvist E 1981 *Surf. Sci.* **105** L288
- [37] Chang S L and Thiel P A 1987 *Phys. Rev. Lett.* **59** 296
- [38] Chang S L, Sanders D E, Evans J W and Thiel P A 1988 *Structure of Surfaces II* ed J F van der Veen and M A van Hove (Berlin: Springer)
- [39] Weiss P S and Eigler D M 1992 *Phys. Rev. Lett.* **69** 2240
- [40] Paul W, Heermann D and Desai R 1989 *J. Comput. Phys.* **82** 489
- [41] Evans J W 1991 *Langmuir* **7** 2514
- [42] Jensen I, Fogedby H C and Dickman R 1990 *Phys. Rev. A* **41** 3411
- [43] Albano E V 1992 *Phys. Rev. Lett.* **69** 656
- [44] Köhler J and ben-Avraham D 1991 *J. Phys. A: Math. Gen.* **24** L621
- [45] ben-Avraham D and Köhler J 1992 *J. Stat. Phys.* **65** 839
- [46] Jensen I and Dickman R 1993 *Phys. Rev. E* **48** 1710
- [47] Grassberger P 1989 *J. Phys. A: Math. Gen.* **22** 3673
- [48] Janssen H K 1981 *Z. Phys. B* **42** 151
- [49] Grassberger P 1982 *Z. Phys. B* **47** 365
- [50] Grinstein G, Lai Z W and Browne D A 1989 *Phys. Rev. A* **40** 4820
- [51] Bunde A, Herrmann H, Margolina A and Stanley H 1985 *Phys. Rev. Lett.* **55** 653
- [52] Fisher M, Ma S and Nickel B 1972 *Phys. Rev. Lett.* **29** 917
- [53] Albano E 1991 *J. Phys. A: Math. Gen.* **24** 3351
- [54] Albano E V 1994 *J. Phys. A: Math. Gen.* **27** 3751