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Finite Size Scaling in the Heterogeneous Reaction $2A + B_2 \longrightarrow 2AB$

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Abstract

In the present paper we extend the exact solution previously obtained for the heterogeneous catalytic reaction $2A+B_2 \rightarrow 2AB$ on small 2×2 domains, to arbitrary lattice sizes $(N \times N)$ and calculate the average number of reactive steps necessary to poison the lattice first,$< t >$. We determine $< t >$ as a function of N through Monte Carlo simulations previously contrasted with the exact solution in 2×2 lattices. We show that $< t >$ follows a power law with N, without appreciable transient behaviors, and a scale factor (ν) dependent on the two parameters of the model, the sticking coefficient probability s and the desorption probability p_d. The dependence of ν on both s and p_d is determined.

1 Introduction

Catalytic reactions have been extensively studied by the surface science community mainly on extended single crystal surfaces. Recent interest has turned to the analysis of reactions in nanoscale systems, e.g., on supported metal clusters or on metal field emitter tips (FET's) with facet linear dimensions of 10 nm. In these systems, fluctuation effects occur specifically due to their small size, and understanding the kinetics of the reactions becomes of both theoretical and practical importance [1-6].

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In recent years we have made a considerable effort to develop analytical methods to find exact solutions in small domains to different problems dealing with adsorption processes in two-dimensional lattices [7-10,13,14]. In [9] we reported scaling behaviors in random sequential adsorption (RSA) processes of β-bell particles ($\beta > 1$), related to configurational correlations. This power-law behavior was observed, after a transient, at large lattice sizes.. The heterogeneous reaction $2A + B_2 \to 2AB$ was exactly solved on a small lattice in [11,12,15]. We considered a generic bimolecular Langmuir-Hinshelwood reaction over a single-crystal catalyst and this model, which we designated AB_2 model, was exactly solved to calculate magnitudes such as the average reaction rate, the average coverages, and the *average deactivation time* $< t >$ (average number of reactive steps necessary to poison the lattice first). The AB_2 model includes adsorption and desorption of the reactants, surface reaction between adsorbed species, and desorption of the products. Diffusion processes of adsorbed species or interactions between adatoms have not been included for simplicity [16-18]. This allows us to reduce the number of adjustable parameters of the model, although it does not alter the main achievement of the work, which is predicting the general aspects of the solution in large domains from the exact solution in small domains. Diffusion may be included, for example, by replacing the absolute certainty of whether one species (the mobile one) will be present or not in a neighboring site with an average value inversely proportional to the species mobility.

The AB_2 model has two parameters s and p_d, which vary between 0 and 1, and all the quantities of interest are expressed in terms of s and p_d. For $< t >$ we showed that the dependence s and *pd* is polynomial and can be exactly calculated on a small 2×2 domain [12, 15]. In the present paper, we analyze the dependence of $< t >$ on $N > 2$, and show that $< t >$ follows a scaling law behavior with a scale factor depending on s and *pd*. We show that there are no transient behaviors to the scaling law, and therefore the AB_2 model can be solved exactly for any lattice size, knowing the exact solution in 2×2 domains and the scale factor. The paper is organized as follows: in Section 2 a review of the model reaction and its exact solution on a small lattice is given [11,12,15]; in Section 3 results of Monte Carlo simulations are presented, and then conclusions are summarized.

2 The Model

The heterogeneous reaction model proceeds through a Langmuir-Hinshelwood mechanism

$$
\begin{aligned}
A_{(g)} + * &\longrightarrow A^* & k_a, s \quad (1)\\
A^* &\longrightarrow A_{(g)} + * & k_d \quad (2)\\
B_{2(g)} + 2* &\longrightarrow 2B^* & k_a, s \quad (3)\\
B^* + B^* &\longrightarrow B_{2(g)} + 2\,* & k_d \quad (4)\\
A^* + B^* &\longrightarrow AB_{(g)} + 2\,* & k_r \quad (5)
\end{aligned}
$$

where k_a, k_d and k_r are the rate constants for adsorption, desorption and reaction, respectively, $*$ denotes a vacant site on the catalyst surface, and s stands for the sticking coefficient probability. The subindex (g) represents a molecule in the gaseous phase, and a superindex $*$ stands for adsorbed species. A molecules require single adsorption sites in order to be adsorbed (see *Eq.2*), whereas B_2 molecules require two neighboring lattice sites to be adsorbed (see *Eq.4*). The reaction step, *Eq. 6,* requires the existence of two neighboring sites occupied by different adsorbates. The desorption of B_2 molecules is a second-order process and requires the existence of two neighboring lattice sites occupied by B^* adsorbates.

In the adsorption steps, *Eqs. 2* and *4*, we introduced a sticking coefficient s, which is the probability of a molecule to be adsorbed after the first impact on an adsorption site. If the sticking coefficient is less than 1 ($s < 1$), there will be the possibility of finding microstates with empty sites. The desorption steps, *Eqs. 3* and *5,* and the reaction step, *Eq. 6,* are controlled by rate equations k_d and k_r.

The desorption probability p_d is one of the adjustable parameters in our model and defines the relative rates of desorption to surface reaction.

$$
p_d = \frac{k_d}{k_r + k_d} \tag{6}
$$

Equal k_d values were assumed for both species. Although this is not the most general situation, it provides a simple illustration of the analytical method developed. Considering different rates of desorption involves introducing an additional adjustable parameter, i.e., the transition probabilities between microstates will depend on three variables.

The second adjustable parameter in our model is the sticking coefficient s (variations of k_a are usually included in s variations). This parameter stands for the adsorption probability of a gaseous molecule on the substrate surface, after the first impact. Again, equal initial partial pressures of the reactants were assumed to simplify the model by decreasing the number of adjustable parameters to be used.

The exact solution of this model was obtained in [11], [12] on a 2×2 lattice that was assumed to be uniform. Periodic boundary conditions were imposed and equal values of partial pressure were chosen for reactants A and B_2 so that $p_A + p_{B_2} = 1$. With these conditions there are 21 different microstates with degeneracies that have been both determined in [11], and [12]. To calculate $< t >$, we must evaluate the probability of arriving at microstate i in k steps without previously visiting a nonreactive microstate. There is a probability P_{ij} for the transition from states i to j, and the probability of arriving first at microstate i in k steps is e_{ik} where

if $k = 0$,

$$e_{i0} = p_i, \qquad i = 1, 2, ..., 21 \tag{7}$$

if $k > 0$,

$$e_{ik} = \sum_j e_{jk-1} P_{ji} \tag{8}$$

The summation is restricted to reactive microstates because we are interested in knowing $< t >$, and its dependence on p_d and s.

Let U_k be the probability of arriving first at a nonreactive microstate *in* k steps, visiting only reactive states in the previous $k - 1$ steps,

$$U(k) = \sum_{j*} e_{j*k} \tag{9}$$

where the summation is restricted to nonreactive microstates. The $< t >$ is

$$< t >= \sum_{k=0}^{\infty} kU(k) \tag{10}$$

The standard deviation of $< t >$, σ is given by

$$\sigma = \sum_{k=0}^{\infty} (k- < t >)^2 U(k) \tag{11}$$

Note that $< t >$, as defined by *Eq. 10,* is the average number of reactive states necessary to poison the lattice first. As the reaction considers desorption processes, it does no stop after this type of event and, therefore, the concentration of products fluctuates over time.

The $< t >$ is independent of the initial distribution of microstates, it is a characteristic time of the reaction and its determination may be important when a constant flow of products is required.

Figure 1 shows the dependence of $< t >$ on s and p_d, as was determined in [12].

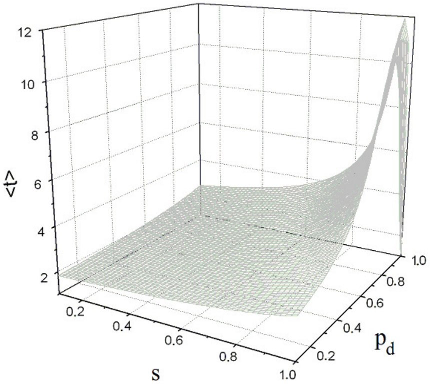

Figure 1. Dependence of $< t >$ on s and p_d. Exact solution of the AB_2 model on a 2×2 lattice with periodic boundary conditions [12].

3 Results and Conclusions

Monte Carlo simulations were performed to study the reaction characteristics on larger lattices, and $< t >$ was calculated in $N \times N$ lattices, with $2 < N < 32$.

As N increases, both $< t >$ and σ (Eq. 11) become larger because the number of reactive states increases. This results in a considerable increase in calculation time, but also the fluctuations become larger, and therefore $< t >$ must be calculated over a considerable number of independent realizations. For $N = 2$, the average was performed on 500,000 independent simulations, and the error in $< t >$ was less than 0.05%. For $N = 16$ this number was reduced to 50,000, still with good results, that is, the error in the calculation of $< t >$ was less than 0.2%. The computing time becomes prohibitive for $N > 32$.

In [12] we showed that the dependence of $< t >$ on s and p_d for arbitrary values of N is qualitatively similar to that obtained analytically for the 2×2 lattice (Fig. 1); $< t >$ exhibits a maximum ($< t >_{max}$) at $s = s_m$ and $p_d = p_{dm}$. In general, $< t >_{max}$ increases with N, while s_m and p_{dm} both decrease with the increase of N. In this work we further explore this dependence on N.

Figure 2 shows the $< t >$ dependence on N for different values of s and p_d. A finite size scaling behavior is observed, which can be expressed in terms of $N = 2$ exact solution as:

$$< t >_N = < t >_2 \left[\frac{N}{2}\right]^v \tag{12}$$

Eq. 12 is valid because there are no appreciable transient behaviors toward the scaling law. The scale factor v depends on s and p_d and thus, given this dependence, the AB_2 model is exactly solved for arbitrary lattice sizes and any value of the adjustable parameters.

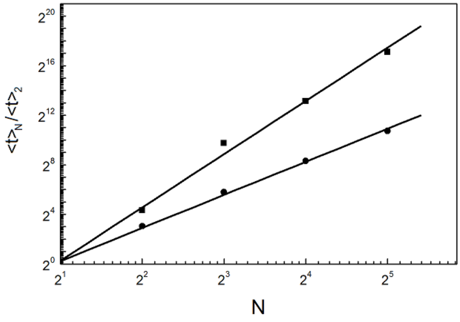

Figure 2. Finite size scaling for $\frac{<t>_N}{<t>_2}$ at two different values of the adjustable parameters (s, pd). Circles: $s = 0$, $pd = 0$, squares: $s = 0.3$, $pd = 0$.

Table 1 shows v as a function of s and p_d as was obtained by adjusting Eq. 12 to the Monte Carlo simulations by the least squares method as in Fig. 2.

The error indicated in parentheses affects the last significant digit of v, and is the standard deviation calculated from an analysis of variance (ANOVA). The scale factor v has a nonmonotonic behavior, strongly influenced by s and less by p_d. Intermediate values of s increase the number of possible ways in which adsorbates can be arranged

Table 1. The values of v as a function of s and p_d obtained by adjusting Eq. 12 to Monte Carlo simulations. The errors appear in brackets.

$p_d \setminus s$	0	0.1	0.2	0.3	0.4	0.5	0.6	0.7	0.8	0.9	1.0
0	2.9(1)	3.30(2)	3.8(2)	4.4(4)	4.7(5)	4.9(4)	4.8(2)	4.7(1)	4.7(1)	4.7(1)	4.5(1)
0.1	2.9(1)	3.27(2)	3.9(2)	4.5(5)	5.0(5)	5.1(4)	4.9(1)	4.73(2)	4.5(2)	4.4(3)	4.3(1)
0.2	2.9(1)	3.27(2)	3.9(2)	4.7(5)	5.3(5)	5.4(6)	5.2(3)	4.91(1)	4.5(2)	4.2(3)	4.0(1)
0.3	2.9(1)	3.27(2)	3.9(2)	4.8(6)	6(1)	6(1)	5.7(5)	5.2(1)	4.6(1)	4.5(3)	3.8(1)
0.4	2.9(1)	3.28(1)	4.0(3)	5.0(6)	6(1)	6(1)	6(1)	5.6(4)	4.8(1)	4.1(3)	3.6(1)
0.5	2.9(1)	3.29(1)	4.0(3)	5.1(7)	6(1)	7(1)	7(1)	6.0(5)	5.0(1)	4.1(2)	3.5(1)
0.6	2.9(1)	3.30(1)	4.0(3)	5.2(7)	6(1)	7(1)	7(1)	6.5(5)	5.3(3)	4.2(1)	3.4(1)
0.7	2.9(1)	3.34(2)	4.0(3)	5.4(8)	7(1)	8(1)	8(1)	7(1)	5.6(5)	4.2(1)	3.2(1)
0.8	3.0(1)	3.37(1)	4.1(3)	5.5(9)	7(1)	8(1)	8(1)	7(1)	6.0(5)	4.3(1)	3.1(1)
0.9	3.0(1)	3.44(1)	4.2(3)	5.8(9)	8(1)	9(1)	9(1)	8(1)	6.4(5)	4.5(3)	3.0(1)
1.0	3.0(1)	3.57(1)	4.5(2)	6.5(5)							

on the surface, widening the distribution function of microstates. Though this scale behavior was calculated only for $< t >$, it could depend only on the final distribution of microstates, and be used for any magnitude associated with this reaction. Then one should study the characteristics of the final microstate distribution. However, as the size of the surface increases, the number of microstates increases dramatically, and their analytical determination becomes extremely difficult. Alternatively, a similar behavior could be expected for all the magnitudes related to the final distribution of microstates. There are studies in progress at La Plata to unravel this challenge.

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References

[1] D. J. Liu, J. W. Evans, Fluctuations and patterns in nanoscale surface reaction systems: Influence of reactant phase separation during CO oxidation, *Phys. Rev. B* **75** (2007) #073401.

[2] V. Skakauskas, P. Katauskis, On the kinetics of the Langmuir-type heterogeneous reactions, *Nonlin. Anal. Modell. Control* **16** (2011) 467–476.

[3] A. V. Zhdanova, Simulation of the kinetics of rapid catalytic reactions on ultrasmall metal particles, *Phys. Rev. B* **63** (2001) #153410.

[4] V. P. Zhdanov, B. Kasemo, Simulations of the reaction kinetics on nanometer supported catalyst particles, *Surf. Sci. Rep.* **39** (2000) 25–104.

[5] Y. Suchorski, J. Beben, E. W. James, J. W. Evans, R. Imbihl, Fluctuation-induced transitions in a bistable surface reaction: catalytic CO oxidation on a Pt field emitter tip, *Phys. Rev. Lett.* **82** (1999) 1907–1910.

[6] Y. Suchorski, J. Beben, R. Imbihl, E. W. James, D-J Liu, J. W. Evans, Fluctuations and critical phenomena in catalytic CO oxidation on nanoscale Pt facets, *Phys. Rev. B* **63** (2001) #165417.

[7] A. E. Bea, A. V. Ranea, I. M. Irurzun, E. E. Mola, Kinetics of immobile adsorption of linear molecules on a two-dimensional lattice, *Chem. Phys. Lett.* **401** (2005) 342–346.

[8] A. E. Bea, I. M. Irurzun, E. E. Mola, How many langmuirs are required for monolayer formation? *Langmuir* **21** (2005) 10871–10873.

[9] A. E. Bea, I. M. Irurzun, E. E. Mola, Scaling properties in the average number of attempts until saturation in random sequential adsorption processes, *Phys. Rev. E* **73** (2006) #051604.

[10] I. M. Irurzun, V. A. Ranea, E. E. Mola, Branch counting probability approach to random sequential adsorption, *Chem. Phys. Lett.* **408** (2005) 19–24.

[11] P. Bergero, V. Pastor, I. M. Irurzun, E. E. Mola, The heterogeneous catalytic reaction $2A + B_2 \rightarrow 2AB$ exactly solved on a small lattice, *Chem. Phys. Lett.* **449** (2007) 115–119.

[12] V. E. Pastor, P. L. Dammig Quiña, L. M. Salvatierra, I. M. Irurzun, E. E. Mola, Average deactivation time of the heterogeneous reaction $2A + B_2 \rightarrow 2AB$, *MATCH Commun. Math. Comput. Chem.* **71** (2014) 47–56.

[13] P. L. Dammig Quiña, V. E. Pastor, I. M. Irurzun, E. E. Mola, Congurational degeneracy of a set of dipoles in a quasi-two-dimensional system, *J. Math. Chem.* **48** (2010) 592–600.

[14] P. L. Dammig Quiña, I. M. Irurzun, E. E. Mola, Congurational Entropy of a Set of Dipoles Placed on a Two-dimensional Lattice, *P*hysica A Stat. Mech. App. **466** (2017) 435–439.

[15] V. E. Pastor, *PhD Thesis,* Faculty of Sciences, La Plata University, La Plata, Argentina, 2012.

[16] J. W. Evans, D. J. Liu, Statistical mechanical models for dissociative adsorption of O2 on metal(100) surfaces with blocking, steering, and funneling, *J. Chem. Phys.* **140** (2014) #194704.

[17] W. Kappus, Adatom pair distribution up to half coverage: O-Pd(100), *Surf. Sci.* **691** (2020) #121465.

[18] D. J. Liu, J. W. Evans, Realistic multisite lattice-gas modeling and KMC simulation of catalytic surface reactions: Kinetics and multiscale spatial behavior for CO-oxidation on metal (100) surfaces, *Prog. Surf. Sci.* **88** (2013) 393–521.