

**One-dimensional diffusion: Discrepancy between exact results and Monte Carlo calculations**

J. J. Torrez Herrera, G. A. Ranzuglia, S. J. Manzi, and V. D. Pereyra

*Departamento de Física, Instituto de Física Aplicada (INFAP) – Consejo Nacional de Investigaciones Científicas y Técnicas (CONICET), Universidad Nacional de San Luis, Chacabuco 917, 5700 San Luis, Argentina*

(Received 18 May 2011; revised manuscript received 26 September 2011; published 7 November 2011)

The exact expression for the collective diffusion coefficient in one dimension, obtained by Payne and Kreuzer [Phys. Rev. B. **75**, 115403 (2007)], is compared with Monte Carlo simulation. Different hopping kinetics are analyzed. For initial- and final-state interaction kinetics no anomalies are observed. However, for the so-called interaction kinetics where both initial- and final-state interactions are involved, it is shown that even when the transition rates satisfy the principle of detail balance, additional constraints are necessary to guarantee the diffusion of particles. These restrictions give rise to a phase diagram that determines the regions where the exact solution of the diffusion coefficient seem to be not physically sound. The Monte Carlo simulation allows us to analyze the mechanism of diffusion in these regions, where in some cases the simulation does not match the exact solution. A possible explanation is presented.

DOI: [10.1103/PhysRevE.84.051102](https://doi.org/10.1103/PhysRevE.84.051102)

PACS number(s): 05.50.+q, 68.43.De, 68.43.Jk

**I. INTRODUCTION**

Theoretical description of the diffusion process is a complicated many-body problem and various approaches have been applied to it, ranging from analytic ones based on master, Fokker-Planck, or Kramers equations, to numerical Monte Carlo simulations. An important background is provided in various reviews [1–7] and original papers [8–16]. In addition to the intrinsic interest, the general results for the one-dimensional (1D) diffusion may be useful for applications (e.g., for describing adsorbate diffusion along steps [17] or on carbon nanotubes [18]).

The kinetic lattice gas model (KLG) is usually the adequate background to describe diffusion of individual or collective motion of atoms in one-, two-, or three-dimensional systems. This approximation can be used when the potential energy for particle motion is determined by a substrate and lateral particle-particle interactions. Often the particle-substrate interaction is sufficiently strong, particles are located primarily at the potential wells formed by the substrate, and there are appreciable activation barriers for jumps of particles between the wells. For this description the usual starting point is the master equation with the hopping between lattice sites treated as a Markovian process (i.e., the residence time at sites is long compared to the time of individual hops). This is also the easiest route to incorporate the effects of multiple binding sites within cells and particle interactions, both hardcore within cells and short range between them. In the case of surface diffusion such interactions lead to a strong dependence of the diffusivity on the coverage of the adspecies. The dynamics in this kinetic lattice gas model are usually simplified to the specification of transition probabilities with a hopping rate, but modified by interactions with neighboring particles in the initial and final configurations, leading to vastly different diffusion behavior.

A fairly general and relatively simple expression for the chemical diffusion coefficient was phenomenologically proposed by Reed and Ehrlich [1], the so-called Reed-Ehrlich (RE) factorization, where a simple expression for the chemical diffusion coefficient was proposed as a product of thermodynamic and kinetic or dynamic factors. Physically,

diffusion jumps represent the simplest Arrhenius processes. Such processes are usually described by the transition state theory (TST) [13,14] (as well as other surface processes [13–15]). In particular, it was shown [13,14,16] that following TST one can derive the RE expression for the diffusion coefficient.

A rather general approach has recently been proposed by Payne and Kreuzer (PK) [19] for one-dimensional lattice gas. They have exactly corroborated the RE factorization [1] for any range of interactions and for any form of the jump rates that satisfies detailed balance. The method of gradient expansion of the local microscopic particle current used by PK has been extended to 2D systems, where they have shown, using transfer matrix methods (TMM), that the RE factorization is not universal and does not apply (e.g., for generalized hopping kinetics where initial- and final-state interactions are involved, such as saddle point interactions [20]).

In the method introduced in Ref. [19], the transition probabilities are written as an expansion of the occupation configurations of all neighboring sites. Since the detailed balance principle determines half of the coefficients that arise from the expansion, it is necessary to introduce *ad hoc* a dynamic scheme to get the rest of them. However, for the principle of detailed balance, it is a necessary but not sufficient condition to have an acceptable physical behavior of the diffusion coefficient and additional constraints on the jump rates must be introduced, as shown in Ref. [21]. Specifically, for the so-called interaction kinetics where both initial- and final-state interactions are involved, it is shown that, even when the transition rates satisfies the principle of detail balance, there are certain values of the parameters for which the diffusion coefficient is negative. As a consequence, a phase diagram that determines the regions where the exact result for the diffusion coefficient is positive, has been obtained.

In the present paper, a Monte Carlo simulation to analyze the diffusion process is proposed. The simulation gives rise to a deeper understanding of the mechanism of diffusion, particularly in the forbidden region of the phase diagram. The comparison between the exact solution and numerical results is analyzed and a possible explanation is given.

The outline of the paper is as follows: in Sec. II a brief description of the model and the exact results is presented; in Sec. III, the Monte Carlo simulation scheme of the diffusion process is described; in Sec. IV, the results are presented and discussed. Finally, Sec. V concludes the paper.

## II. THE KINETIC LATTICE GAS MODEL

Let us consider a system composed of  $N$  sites in one or two dimensions. To describe the state of the system one introduces microscopic occupation numbers  $n_i = 1$  or  $0$ , depending on whether the sites are occupied by an adsorbed particle or not. There are  $2^N$  microstates  $\mathbf{n} = (n_1, n_2, \dots, n_N)$  given by sequence of zeros and ones. To introduce the dynamics of the system one writes down a model Hamiltonian

$$H = E_s \sum_i n_i + V \sum_{i,a} n_i n_{i+a} + \dots, \quad (1)$$

where  $V$  is the adsorbate-adsorbate interaction energy between nearest-neighbor  $NN$  particles,  $E_s$  is the interaction between the substrate and the adatom, and  $(i, j)$  represents pairs of  $NN$  sites. Longer range interactions, like nearest-neighbor,  $NNN$ , and trio interactions can be included.

Let us introduce a function,  $P(\mathbf{n}, t)$ , which gives the probability that a given microstate  $\mathbf{n}$  of the lattice gas is realized at time  $t$ , and the transition probability,  $W(\mathbf{n}; \mathbf{n}')$ , per unit time as the probability to go from a state  $\mathbf{n}'$  to  $\mathbf{n}$ . Treating hopping as a Markov process  $P(\mathbf{n}, t)$  must satisfy a master equation

$$\frac{dP(\mathbf{n}; t)}{dt} = \sum_{\mathbf{n}'} [W(\mathbf{n}; \mathbf{n}')P(\mathbf{n}'; t) - W(\mathbf{n}'; \mathbf{n})P(\mathbf{n}; t)]. \quad (2)$$

To ensure the approach to equilibrium in an isolated system each term in the sum must satisfy detailed balance

$$W(\mathbf{n}'; \mathbf{n})P_{\text{eq}}(\mathbf{n}) = W(\mathbf{n}; \mathbf{n}')P_{\text{eq}}(\mathbf{n}'), \quad (3)$$

where

$$P_{\text{eq}}(\mathbf{n}) = \frac{e^{-[H(\mathbf{n}) - \mu N(\mathbf{n})]/k_B T}}{\Xi}. \quad (4)$$

Here,  $k_B$ ,  $T$ , and  $\mu$ , are the Boltzmann constant, the temperature, and the chemical potential, respectively.  $P_{\text{eq}}$  is the equilibrium probability and  $\Xi$  is the grand canonical partition function given by

$$\Xi = \sum_{\mathbf{n}} e^{-[H(\mathbf{n}) - \mu N(\mathbf{n})]/k_B T}. \quad (5)$$

In the absence of adsorption and desorption the number of adparticles,  $N(\mathbf{n})$ , is fixed and the form of  $W(\mathbf{n}'; \mathbf{n})$  depends on the jump scheme exclusively. When diffusion results from the hopping of single particles from an occupied site to a neighboring unoccupied site, one can write this transition probability as

$$W_{\text{diff}}(\mathbf{n}'; \mathbf{n}) = \sum_{i,a} [W_i^> + W_{i+a}^<] \times \delta_{n_i'}^{1-n_i} \delta_{n_{i+a}'}^{1-n_{i+a}} \prod_{l \neq i, i+a} \delta_{n_l'}^{n_l}, \quad (6)$$

where

$$W_i^> = J_0 n_i (1 - n_{i+1}) [(1 - n_{i-1})(1 - n_{i+2}) + (1 + A_1)n_{i-1} \times (1 - n_{i+2}) + (1 + B_1)(1 - n_{i-1})n_{i+2} + (1 + A_1 + B_1 + C_{11})n_{i-1}n_{i+2}]. \quad (7)$$

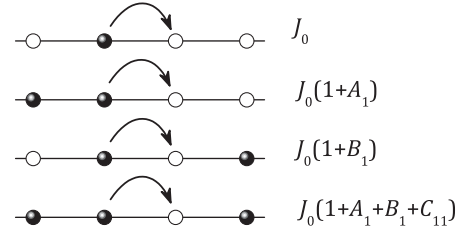


FIG. 1. The four relevant hopping processes and their rates for a one-dimensional lattice gas with nearest-neighbor interactions.

In the last equation, the probability to jump to the right from site  $i$  to  $i + 1$  is written in terms of the occupation configurations of all neighboring sites (a similar expression can be obtained for  $W_i^<$ ). For a better comprehension of each term in the last equation, see the scheme in Fig. 1. The first term in Eq. (2) represents the jump of a particle that is isolated before and after the jump, with a rate  $J_0$ . The second term represents the separation of a particle from a neighbor with a rate  $J_0(1 + A_1)$ ; the particle has no neighbors after the event. The third term represents the converse of the above process, with a rate  $J_0(1 + B_1)$ . The last term represents the exchange of a particle and vacancy between two neighbors with rate  $J_0(1 + A_1 + B_1 + C_{11})$ . The elementary hopping rate,  $J_0$ , usually has the Arrhenius form.

Payne and Kreuzer have exactly demonstrated the RE factorization [1,19,20]

$$D(\theta, T) = \chi^{-1} \langle W \rangle, \quad (8)$$

where  $\langle W \rangle = \frac{1}{2} \langle W_i^> + W_{i+1}^< \rangle$  is the average transition rate for a 1D system and  $\chi^{-1}$  is the inverse of the susceptibility defined as

$$\chi^{-1} = \frac{\partial \beta \mu}{\partial \theta} = [\alpha \theta (1 - \theta)]^{-1}, \quad (9)$$

where  $\theta$  is the coverage and  $\alpha$  is related to the chemical potential,  $\mu$ , by

$$\exp[\beta \mu] = \left( \frac{\alpha - 1 + 2\theta}{\alpha + 1 - 2\theta} \right) \exp[\beta V], \quad (10)$$

where  $\beta = 1/k_B T$ .

By using the same methodology proposed by PK and after expanding the average transition rate in terms of the occupation probabilities, one can finally write the collective diffusion coefficient in a diagrammatic form as

$$D(\theta, T) = D_0 \chi^{-1} [\langle \bullet \circ \rangle + A_1 \langle \bullet \bullet \circ \rangle + B_1 \langle \bullet \circ \bullet \rangle + C_{11} \langle \bullet \bullet \circ \bullet \rangle], \quad (11)$$

where

$$\langle \bullet_i \circ_{i+1} \dots \bullet_{i+k} \rangle = \sum_{\mathbf{n}} n_i (1 - n_{i+1}) \dots n_{i+k} P(\mathbf{n}; t). \quad (12)$$

Here  $P(\mathbf{n}, t)$  represents the probability that a given microscopic configuration  $\{\mathbf{n}\} = (n_1, n_2, \dots, n_N)$  is realized at time  $t$ , where  $N$  is the total number of sites in the line.

The detailed balance principle puts one condition on the three coefficients, namely,

$$(1 + A_1) = (1 + B_1) e^{\beta V}. \quad (13)$$

Various combinations of these coefficients allow one to describe different scenarios of diffusion involving initial and final kinetics, including all types of combinations of both initial and final kinetics, such saddle point kinetics and TST kinetics [19,21]. To preserve particle-hole symmetry in the jumping process, the third coefficient  $C_{11}$  must be considered. In this case, the first and fourth terms in Eq. (2) must be the same, which requires that  $A_1 + B_1 + C_{11} = 0$ .

PK have considered different cases [19], the first one (case I), is the initial-state interaction, characterized by  $B_1 = C_{11} = 0$ . The second kinetic scheme is the final-state interaction, where  $A_1 = C_{11} = 0$  (case II).

To analyze the hopping kinetics involving initial- and final-state interactions, PK have proposed the following linear relation between the coefficients

$$A_1 = -\gamma B_1. \quad (14)$$

Taking into account the detailed balance principle, they obtain

$$B_1 = \frac{1 - \exp(\beta V)}{\gamma + \exp(\beta V)}. \quad (15)$$

The parameter  $\gamma$  is considered of order unity by PK. Furthermore, no restrictions are imposed on  $C_{11}$ . Therefore, they have analyzed three different cases, with  $B_1 = -A_1$ : (case III)  $C_{11} = 0$ ; (case IV)  $C_{11} = -A_1$ ; and (case V)  $C_{11} = -B_1$ . As observed in Ref. [19], the behavior of the normalized diffusion coefficient as a function of the coverage is always bigger than unity [ $D(\theta)/D(0) > 1$ ] for repulsive lateral interactions and smaller than unity [ $D(\theta)/D(0) < 1$ ] for attractive lateral interactions, with the exception of case II, where the behavior is the opposite. No phase transitions occur in the 1D systems, therefore the diffusion coefficient should be positive.

No restrictions are imposed by the detailed balance principle on  $\gamma$  [15,21]. Moreover, the behavior of the collective diffusion coefficient, obtained by using Eq. (3), is reasonable for any positive value of  $\gamma$ . However, for negative values of  $\gamma$  there are combinations of parameters  $\gamma$  and  $V$  that lead to

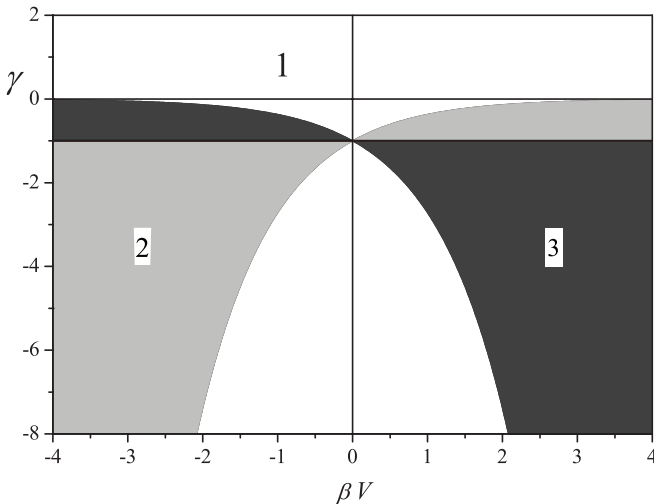


FIG. 2. Phase diagram for  $A_1 = -\gamma B_1$  and  $C_{11} = 0$  showing the different diffusion zones. The white color corresponds to the region A. The light gray corresponds to the region B, while the dark gray corresponds to the region C.

negative diffusion coefficients, at least for certain values of coverage. These values can be represented in a phase diagram as shown in Ref. [21].

The phase diagram (Fig. 2) corresponding to case III contains: i) the allowed region (region 1), where all the rates define for the hopping processes in Fig. 1 are positive; ii) the forbidden region (region 2), where only  $J_0(1 + A_1 + B_1 + C_{11})$  is negative; and iii) the forbidden region (region 3), where  $J_0(1 + A_1)$ ,  $J_0(1 + B_1)$  and  $J_0(1 + A_1 + B_1 + C_{11})$  are negative. Similarly, one can describe the cases IV and V. In what follows, only case III will be considered.

### III. MONTE CARLO SIMULATION

Alternatively, the diffusion process can be calculated by Monte Carlo simulation [22]. The tracer diffusion coefficient,  $D_T$ , is determined from measurement of the mean-square displacements (MSDs)

$$S_T(t) = \sum_{i=1}^N \langle [\mathbf{r}_i(t) - \mathbf{r}_i(0)]^2 \rangle \quad (16)$$

of  $N$  tagged adatoms according to [1,4,23]

$$D_T = \lim_{t \rightarrow \infty} \frac{1}{2dNt} \sum_{i=1}^N \langle [\mathbf{r}_i(t) - \mathbf{r}_i(0)]^2 \rangle. \quad (17)$$

The collective diffusion coefficient can be written, in the framework of the Kubo-Green theory, as

$$D(\theta, T) = \left( \frac{\partial \mu / k_B T}{\partial \ln \theta} \right) D_J = \left[ \frac{\langle \delta N \rangle}{\langle N \rangle} \right]^{-1} D_J, \quad (18)$$

where  $\langle \delta N \rangle$  is the mean-square fluctuation in an area  $A$  containing  $\langle N \rangle$  particles. The jump diffusion coefficient,  $D_J$ , is related to the MSD of the center of mass of the system

$$S_J(t) = \left\langle \left( \sum_{i=1}^N |\mathbf{r}_i(t) - \mathbf{r}_i(0)| \right)^2 \right\rangle \quad (19)$$

by

$$D_J = \lim_{t \rightarrow \infty} \frac{1}{2dNt} \left\langle \left( \sum_{i=1}^N |\mathbf{r}_i(t) - \mathbf{r}_i(0)| \right)^2 \right\rangle. \quad (20)$$

MC results are obtained by performing a random walk of the particles on the line and using Eqs. (9) and (11).

Usually, to obtain  $D_T$  and  $D_J$ , one plots the MSD of the tagged particles and of the center of mass of the system, Eqs. (9) and (11), as function of time in log-log scale. One calculates the slope of the each curve for a very long time. Then, from the intercept, one gets the value of  $D_J$  and  $D_T$  [22]. For normal or gaussian diffusion in a one-dimensional system,  $D_J \propto t$ , while it is demonstrated [24] that  $D_T \propto t^{1/2}$ .

### IV. RESULTS

Next, the comparison between the exact results and MC simulation is presented and discussed. For those values of the parameters  $\gamma$  and  $V$  belonging to region 1, the exact and MC results coincide for the whole range of coverage; starting from

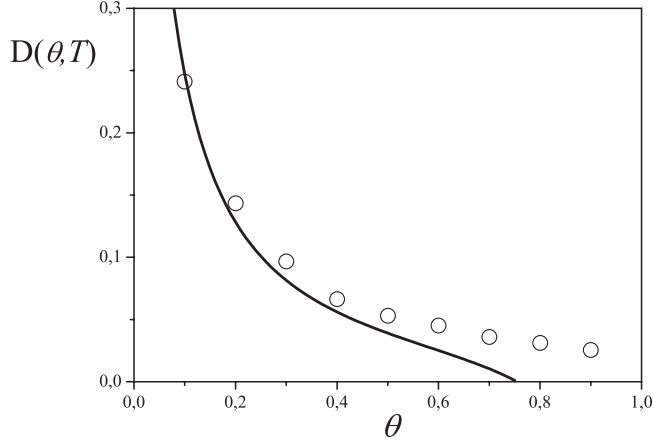


FIG. 3. Collective diffusion coefficient vs  $\theta$  for  $\beta V = -2$  and  $\gamma = -2$ . Solid line corresponds to exact solution given by Eq. (11), while symbols correspond to MC simulation.

an initial equilibrium configuration (the equilibrium is attained by using Kawasaki dynamics) or a random configuration.

For those values of  $\gamma$  and  $V$  belonging to region 2 and 3, the exact results obtained by using Eq. (3) differ, in some cases, from simulations. The reason for these discrepancies is associated with the negative values of the transition rates.

In region 2, Eq. (3) gives negative values for the diffusion coefficients at high coverage (see Fig. 3); this is because  $J_0(1 + A_1 + B_1 + C_{11}) < 0$ . However, if one considers that the transition rates are zero whenever they are negative, the simulations and exact results are in agreement. Here, the initial configuration plays an important role in the simulation. In fact, for coverage,  $\theta > 0.5$ , and considering that only  $J_0(1 + A_1 + B_1 + C_{11}) < 0$ , the diffusion exists when, in the initial configuration: i) two nearest-neighbor sites are empty or ii) an occupied site is surrounded by two empty nearest neighbors. Otherwise, the situation will be similar to case 3, which is discussed in the next paragraph.

In region 3 all the transition rates, except  $J_0$ , are negative, therefore the collective diffusion coefficients are negative for some values of coverage. The Monte Carlo calculations of both  $D_J$  and  $D_T$  coefficients (consequently the collective diffusion coefficient) present a very different behavior. To attain a deeper understanding of the behavior of the system, in Fig. 4 the MSD for the tracer particles for  $\gamma = -2$ ,  $\beta V = 2$ , and  $\theta = 0.2$  is shown. Three well-defined regimes are distinguished: i) a short-times regime, where very few particles collisions have yet occurred, and the particles are diffusing independently of each other; ii) an intermediate-times regime, where the dynamics is dominated by particle collisions; and iii) a long-times regime, where the MSD reaches a saturation value,  $S_T(t \rightarrow \infty) = S_T^{\text{eq}}$ . Since  $J_0(1 + A_1) < 0$ , as soon as two nearest-neighbor sites are occupied, the pair of particles are immobilized, giving rise to a finite number of traps in the system. This problem corresponds to the movement of particles in a box and was addressed for the classical lattice gas system by several authors [24–30]. Recently, the problem of single-file motion in a box has been also addressed [31–33]. Although, in Ref. [25], an analytical solution and the asymptotic limit are obtained for the diffusion of tagged particles in a concentrated lattice gas,

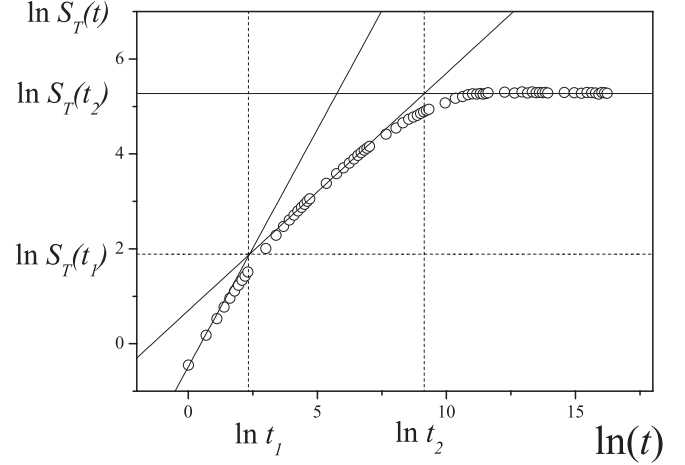


FIG. 4. Mean-square displacement of the tracer particles vs time, for  $\beta V = 2$ ,  $\gamma = -2$ , and  $\theta = 0.2$ . The solid lines correspond to the analytical solution obtained by using Eq. (21).

the problem does not correspond to the present case. This is because, here, there is nonequivalence between the particles and the vacancies. Indeed, because  $J_0(1 + B_1) < 0$  and  $J_0(1 + A_1 + B_1 + C_{11}) < 0$ , the particles behave as dimers (i.e., they have double occupancy). Taking this characteristic into account, one can approximate the three regimes for the MSD by

$$S_T(t) \approx \begin{cases} 2(1 - 2\theta)J_0t & \text{for } t \ll t_1 \\ \frac{2(1-2\theta)}{\theta} \sqrt{\frac{J_0}{\pi}} t^{1/2} & \text{for } t_1 \ll t \ll t_2 \\ S_T^{\text{eq}} & \text{for } t_2 \ll t \end{cases} \quad (21)$$

Clearly, the factor  $(1 - 2\theta)$  represents the available sites on the line. The three regimes are represented by solid lines in Fig. 4. The time  $t_1$  indicates the crossover between the normal diffusion and subdiffusion, while  $t_2$  is the crossover time to saturation. The expression for the crossover time  $t_1$  is

$$t_1 = \frac{1}{J_0\theta^2\pi}. \quad (22)$$

Using combinatorial analysis (see Appendix) the value of  $S_T^{\text{eq}}$  can be analytically obtained. In Table I, a comparison between the saturation values of the MSD for tagged particles obtained by MC simulation and combinatoric analysis, is given. Using the value of  $S_T^{\text{eq}}$  one can obtain the expression for the crossover time  $t_2$  as

$$t_2 = \frac{\theta^2(S_T^{\text{eq}})^2}{4(1 - 2\theta)^2 J_0} \pi. \quad (23)$$

TABLE I. Crossover times and mean-square displacements for the center of mass of the system as a function of coverage.

$\theta$	$\ln(t_2)$	$\ln[S_T(t_2)]$
0.1	12.691	12.499
0.2	9.129	8.823
0.3	6.967	6.240
0.4	5.151	3.799
0.5	3.361	1.303

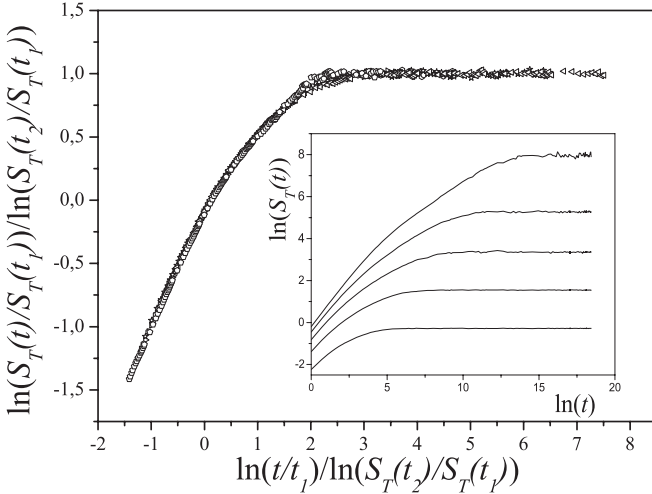


FIG. 5. Collapsed curves corresponding to the mean-square displacement of the tracer particles. In the inset the mean-square displacements of the tracer particles vs time for  $\beta V = 2$ ,  $\gamma = -2$ , are shown (from top to bottom  $\theta = 0.1, 0.2, 0.3, 0.4, 0.5$ ).

Motivated by the results obtained in Ref. [34], and by using the technique developed in Ref. [35], it is possible by using similar scaling arguments to obtain the collapse of the MSD curves. To do that, the two crossover times,  $t_1$  and  $t_2$ , and the corresponding values of the MSD,  $S_T(t_1)$  and  $S_T(t_2)$ , are determined for each curve. Then, all the curves are translated in a log-log plot such that the first crossover point is now located at the origin. This is achieved by plotting  $\ln(\frac{S_T(t)}{S_T(t_1)})$  as a function of  $\ln(\frac{t}{t_1})$ . In the second step both axes are rescaled by the common scale factor  $\lambda = 1/\ln(\frac{S_T(t_2)}{S_T(t_1)})$  such that in the log-log plot the second crossover point is fixed. The scaling can be described by:

$$\frac{\ln\left(\frac{S_T(t)}{S_T(t_1)}\right)}{\ln\left(\frac{S_T(t_2)}{S_T(t_1)}\right)} = F\left[\frac{\ln\left(\frac{t}{t_1}\right)}{\ln\left(\frac{S_T(t_2)}{S_T(t_1)}\right)}\right], \quad (24)$$

where  $F(x)$  is a given scaling function containing the three characteristic regimes. Figure 5 shows how all the data corresponding to the MSD for the tracer particles for  $\gamma = -2$  and  $\beta V = 2$  and different coverages (see the inset of Fig. 5) can be collapsed in a single universal function according to the proposed form, Eq. (12).

Finally, it is possible to use similar arguments of dynamic scaling for the MSD of the center of mass of the system. One

TABLE II. Comparison between the saturation values of the MSD for tagged particles obtained by MC simulation and combinatoric analysis.

$\theta$	$\ln(S_T^{eq})_{MC}$	$\ln(S_T^{eq})_{CA}$
0.1	7.975	7.950
0.2	5.270	5.217
0.3	3.351	3.320
0.4	1.544	1.511
0.5	-0.282	-0.308

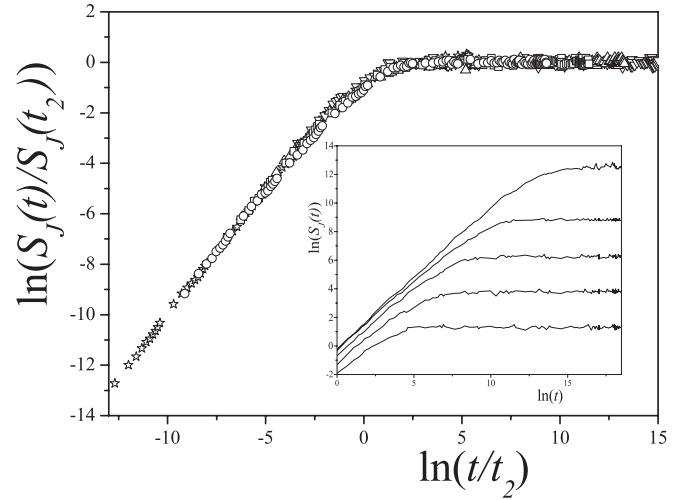


FIG. 6. Collapsed curves corresponding to the mean-square displacement of the center of mass of the system. In the inset the mean-square displacements for the center of mass vs time for  $\beta V = 2$ ,  $\gamma = -2$ , are shown (from top to bottom  $\theta = 0.1, 0.2, 0.3, 0.4, 0.5$ ).

proceeds in the same way as above. Firstly, one determines the saturation values of the MSD  $S_J(t_2)$  and the corresponding crossover time for the saturation  $t_2$  (see Table II), then plotting  $S_J(t)/S_J(t_2)$  as a function of  $t/t_2$  one obtains the collapse of the curves (see Fig. 6).

## V. CONCLUSION

Summarizing, the exact result for diffusion in one dimension, obtained by Payne and Kreuzer, is compared with Monte Carlo simulation. This comparison allows the establishment of the mechanism of the diffusion. In particular, in the forbidden region two well-defined zones are determined as a function of the values of the transition rates. It has been discussed why the PK formula cannot account for the diffusion behavior of the system in the forbidden regions of the phase diagram.

In region 2, one can recover the agreement between the exact results and the simulation by imposing the condition that the transition rates become zero when they take negative values. In region 3, the exact solution predicts that the collective diffusion coefficient is negative for certain values of the coverage. However, the simulation shows that the movement of the particles is very much like the single-file diffusion in a box. Indeed, after equilibrium process, two particles located in nearest-neighbor sites remain in their position for the rest of the diffusion process. The spaces between those pairs of particles are boxes. The size and the number of the boxes depend on the coverage. As is expected, the MSD for tagged or tracer particles presents three diffusion regimes: normal, subdiffusive, and saturation behaviors. Due to the characteristics of the transition rates, the particles move as dimers. An approximate solution for the normal and subdiffusive regimes has been proposed. By combinatorial analysis, the saturation values of the MSD as a function of the coverage for any size of the particle are obtained. These values are in agreement with Monte Carlo simulation. As is expected, for the MSD of the center of mass, only two regimes

are observed: the normal diffusion and the saturation regimen. Collapsing curves are obtained for both the tagged and center of mass mean-square displacement. Finally, it is important to remark that the aim of the present study is to show the mechanisms of diffusion in the forbidden region, which does not contradict the results obtained by Payne and Kreuzer, but are complementary.

#### ACKNOWLEDGMENTS

The authors thank Dr. P. Centres for discussions. This work was partially supported by the CONICET (Argentina).

$$Q_m(s, k) = \frac{\binom{s-1-(m-1)(k-1)}{m-1} \binom{N-s-k+1-\left(\frac{\theta N}{k}-m\right)(k-1)}{\frac{\theta N}{k}-m}}{\binom{N-\frac{\theta N}{k}(k-1)}{\frac{\theta N}{k}}}. \quad (\text{A2})$$

Here,  $\frac{\theta N}{k}$  is the number of  $k$ -mers in the chain. The two factors in the numerator count the number of configurations of all  $k$ -mers to the left and right of the  $k$ -mer  $m$ , respectively, and the denominator counts the total number of configurations on the chain. The mean value and the mean square of the position of the  $k$ -mer  $m$  can be evaluating numerically using the following expressions:

$$\langle r_m \rangle = \sum_{s=km-(k-1)}^{N-\theta N+k(m-1)+1} sa Q_m(s, k) \quad (\text{A3})$$

#### APPENDIX

The analytical procedures to obtain the saturation value,  $S_T^{\text{eq}}$ , are based on the fact that for large times the initial distribution for the position  $\mathbf{r}_m$  of a particle  $m$  becomes uncorrelated from the final distribution. Hence one has

$$\langle [\mathbf{r}_m(t) - \mathbf{r}_m(0)]^2 \rangle = \langle ([\mathbf{r}_m(t) - \langle \mathbf{r}_m \rangle] - [\mathbf{r}_m(0) - \langle \mathbf{r}_m \rangle])^2 \rangle = 2 \langle r_m^2 \rangle - \langle r_m \rangle^2. \quad (\text{A1})$$

The right-hand side of this equation can be evaluated by means of combinatorial analysis. The probability of finding the first component of particle  $m$  of size  $k$  ( $k$ -mer) at site  $s$ , in a chain of  $N$  sites, with  $m \leq s \leq N$ , is given by

and

$$\langle r_m^2 \rangle = \sum_{s=km-(k-1)}^{N-\theta N+k(m-1)+1} s^2 a Q_m(s, k), \quad (\text{A4})$$

where  $a$  is the lattice constant. Finally one may average Eq. (12) over  $m$ . For  $k = 1$  the exact result obtained in Eq. (2.46) of Ref. [25] is reproduced, while for  $k \geq 2$  the exact calculation is rather cumbersome and numerical evaluation of the Eq. (A1) is more appropriate.

- 
- [1] D. A. Reed and G. Ehrlich, *Surf. Sci.* **102**, 588 (1981); **105**, 603 (1981).
- [2] J. W. Haus and K. Kehr, *Phys. Rep.* **150**, 263 (1987).
- [3] S. Havlin and D. Ben-Avraham, *Adv. Phys.* **36**, 695 (1987).
- [4] R. Gomer, *Rep. Prog. Phys.* **53**, 917 (1990).
- [5] A. Danani, R. Ferrando, E. Scalas, and M. Torri, *Int. J. Mod. Phys. B* **11**, 2217 (1997).
- [6] T. Ala-Nissila, R. Ferrando, and S. C. Ying, *Adv. Phys.* **51**, 949 (2002).
- [7] G. Antczak and G. Ehrlich, *Surf. Sci. Rep.* **62**, 39 (2007).
- [8] W. Zwerger, *Z. Phys. B* **42**, 333 (1981); A. V. Myshlyavtsev, A. A. Stepanov, C. Uebing, and V. P. Zhdanov, *ibid.* **52**, 5977 (1995); C. Uebing and V. P. Zhdanov, *Phys. Rev. Lett.* **80**, 5455 (1998); *J. Chem. Phys.* **109**, 3197 (1998); C. Uebing, V. Pereyra, and G. Zgrablich, *Surf. Sci.* **366**, 185 (1996).
- [9] P. Argyrakis, A. A. Chumak, and M. Maragakis, *Phys. Rev. B* **71**, 224304 (2005); **76**, 054209 (2007); P. Argyrakis, M. Maragakis, O. Chumak, and A. Zhugayevych, *ibid.* **74**, 035418 (2006); P. Argyrakis, A. Milchev, V. Pereyra, and K. W. Kehr, *Phys. Rev. E* **52**, 3623 (1995).
- [10] L. Badowski, M. A. Zaluska-Kotur, and Z. W. Gortel, *Phys. Rev. B* **72**, 245413 (2005); M. A. Zaluska-Kotur and Z. W. Gortel, *ibid.* **72**, 235425 (2005); **74**, 045405 (2006); M. Yakes, M. Hupalo, M. A. Zaluska-Kotur, Z. W. Gortel, and M. C. Tringides, *Phys. Rev. Lett.* **98**, 135504 (2007).
- [11] K. Kawazaki, *Phys. Rev.* **145**, 224 (1966).
- [12] Z. Chvoj, *J. Phys. Condens. Matter* **12**, 2135 (2000).
- [13] V. P. Zhdanov, *Elementary Physicochemical Processes on Solid Surfaces* (Plenum, New York, 1991).
- [14] V. P. Zhdanov, *Surf. Sci.* **149**, L13 (1985); **111**, 63 (1981); **111**, L662 (1981); **123**, 106 (1982); **133**, 469 (1983); **157**, L384 (1985); **165**, L31 (1986); **171**, L461 (1986); **209**, 523 (1989); *Surf. Sci. Rep.* **12**, 185 (1991); B. Li, C.-S. Zhang, V. P. Zhdanov, and P. R. Norton, *Surf. Sci.* **322**, 373 (1995); V. P. Zhdanov and B. Kasemo, *ibid.* **412**, 527 (1998).
- [15] S. J. Manzi, R. E. Belardinelli, G. Costanza, and V. D. Pereyra, *Phys. Rev. E* **79**, 021103 (2009); S. J. Manzi, V. J. Huespe, R. E. Belardinelli, and V. D. Pereyra, *ibid.* **80**, 051112 (2009).
- [16] G. S. Bokum, Ya. G. Groda, C. Uebing, and V. S. Vikhrenko, *Physica A* **296**, 83 (2001).

- [17] R. Butz and H. Wargner, *Surf. Sci.* **87**, 85 (1979); M. V. Arena, E. D. Westre, D. E. Brown, J. Kutzner, and S. M. George, *ibid.* **325**, 151 (1995).
- [18] A. Kirakosian, R. Bennowitz, F. J. Himpsel, and L. W. Bruch, *Phys. Rev. B* **67**, 205412 (2003); Y. Gan, J. Kotakoski, A. V. Krasheninnikov, K. Nordlund, and F. Banhart, *New J. Phys.* **10**, 023022 (2008).
- [19] S. H. Payne and H. J. Kreuzer, *Phys. Rev. B* **75**, 115403 (2007).
- [20] S. H. Payne and H. J. Kreuzer, *Phys. Rev. B* **77**, 121403(R) (2008); *J. Phys. Condens. Matter* **21**, 134013 (2009).
- [21] S. J. Manzi, G. A. Ranzuglia, and V. D. Pereyra, *Phys. Rev. E* **80**, 062104 (2009).
- [22] F. M. Bulnes, V. D. Pereyra, and J. L. Riccardo, *Phys. Rev. E* **58**, 86 (1998); A. J. Ramirez-Pastor, T. P. Eggarter, V. D. Pereyra, and J. L. Riccardo, *Phys. Rev. B* **59**, 11027 (1999).
- [23] C. Uebing and R. Gomer, *J. Chem. Phys.* **95**, 7626 (1991); **95**, 7636 (1991); **95**, 7641 (1991); **95**, 7648 (1991); C. Uebing, V. Pereyra, and G. Zgrablich, *Surf. Sci.* **366**, 185 (1996); *J. Chem. Phys.* **106**, 9320 (1997).
- [24] T. E. Harris, *J. Appl. Prob.* **2**, 323 (1965).
- [25] H. van Beijeren, K. W. Kehr, and R. Kutner, *Phys. Rev. B* **28**, 5711 (1983).
- [26] P. M. Richards, *Phys. Rev. B* **16**, 1393 (1977).
- [27] P. A. Fedders, *Phys. Rev. B* **17**, 40 (1978).
- [28] A. Arratia, *Ann. Probab.* **11**, 362 (1983).
- [29] V. Pereyra, A. Milchev, and V. Fleurov, *Phys. Rev. E* **50**, 4636 (1994); G. Zgrablich, V. Pereyra, M. Ponzi, and M. Marchese, *AICHE J.* **32**, 1158 (1986).
- [30] R. Kutner, H. van Beijeren, and K. W. Kehr, *Phys. Rev. B* **30**, 4382 (1984).
- [31] M. Kollmann, *Phys. Rev. Lett.* **90**, 180602 (2003).
- [32] L. Lizana and T. Ambjörnsson, *Phys. Rev. Lett.* **100**, 200601 (2008).
- [33] T. Ambjörnsson, L. Lizana, M. A. Lomholt, and R. J. Silbey, *J. Chem. Phys.* **129**, 185106 (2008).
- [34] P. M. Centres and S. Bustingorry, *Phys. Rev. E* **81**, 061101 (2010).
- [35] Y.-L. Chou and M. Pleimling, *Phys. Rev. E* **79**, 051605 (2009).