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Surface Science 479 (2001) 224–230

SURFACE SCIENCE

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Effects of correlations and lattice gas restriction on the collective diffusion

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Received 6 September 2000; accepted for publication 27 February 2001

Abstract

The combined effects of correlations and lattice gas restriction on the collective diffusion behavior of one-dimensional concentration profiles are studied. Correlations are introduced as a persistent or anti-persistent movement in the individual random walk performed by the diffusing particles. The value of the diffusivity as a function of correlation is obtained for the continuous case through a new and simple analytical method. For the single occupancy (lattice gas) case, the collective diffusion coefficient is calculated by using the Boltzmann–Matano method. It is shown that the collective behavior of the system makes the concentration profiles not to scale, and the values of the diffusion coefficient become dependent on the type and amount of correlation and on the local concentration when the single occupancy restriction is present. © 2001 Elsevier Science B.V. All rights reserved.

Keywords: Computer simulations; Models of surface kinetics; Diffusion and migration

1. Introduction

From an experimental point of view, the measurement of surface diffusion properties is usually done by following the time evolution of initially non-uniform concentration profiles. The analytical theory behind this measurement is well established. The value of the collective diffusion coefficient or diffusivity $D(c)$ can be obtained from the solution of the linear diffusion equation

$$\frac{\partial C(x,t)}{\partial t} = \frac{\partial}{\partial x}\left[D(c)\frac{\partial C(x,t)}{\partial x}\right]. \tag{1}$$

As long as the scaling condition $C(x,t) = C(x/t^{1/2})$ is fulfilled an expression for the diffusion coefficient can be obtained from Eq. (1) as

$$D(c) = -\frac{1}{2t}\left[\int_0^C x\,\mathrm{d}C'\right]\left[\frac{\mathrm{d}C'}{\mathrm{d}x}\bigg|_C\right]^{-1}, \tag{2}$$

which is known as the Boltzmann–Matano (BM) method [1]. For an initial one-dimensional (1d) step concentration profile, $C(x,0) = C_0$ for $x < 0$, $C(x,0) = 0$ for $x > 0$, the analytical solution of Eq. (1) can be written as

$$C(x,t) = \frac{C_0}{2}\left(1 - \operatorname{erf}\frac{x}{2\sqrt{Dt}}\right), \tag{3}$$

for which the scaling condition is fulfilled and then the BM method can be applied.

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PII: S0039-6028(01)00980-3

Recently, it has been shown that the BM method is not to be directly applicable in all situations. In Ref. [2], the limitations of the method has been analyzed, in two dimensions, for an initial concentration profile consisting in a square patch. Also, in the same reference, it is shown that the diffusion coefficient is sensitive to the presence of interactions among the diffusing particles. Motivated by those results, we consider it worth to analyze through the BM method other microscopic behavior of the diffusion particles that might influence the value of the collective diffusivity. It is worth to mention that there are many situations in which the microscopic movement of the particles is correlated. The behavior of the diffusivity in cases in which interactions are relevant has been recently studied [3,4]. Results in those references are based in a well known fact that, in the presence of interactions, a correlation in the movement of each diffusing particle appears [5].

On the other hand, there are many other situations in which correlations are directly incorporated in the microscopic movement of individual particles. In this sense, several models have been introduced (for instance, see Ref. [6]). Diffusion with correlation implies a 'memory' of the moving particle on previous events. Thus, the action of a moving particle at each step depends on its previous trajectory steps. In these situations, although following a random walk (RW) movement, the particles may tend to keep moving in the same direction of the previous jump (persistence) or in the opposite direction of the previous jump (antipersistence). For example, in the course of studies of microscopic motion of particles, it was shown that a particle may persist moving in the same direction after a collision (see Ref. [2] and references therein). From a theoretical point of view, these correlations have been modeled by a certain type of RWs in which the memory of the last jump is not lost after each step, but only after a finite number of steps [7]. In this sense, the inclusion of persistence (or anti-persistence) in the movement of an individual walker gives rise to a definite nonlinear time evolution of the mean square displacement [8].

Correlation (or memory) accounts for the fact that the particle may possess an inertia if it persists to move in the same direction for a time comparable to the observation time. The appearance of backward correlations is also possible. In this case, the particle will tend to make a movement in the direction opposite to the most recent step. As an example of a possible 1d model displaying correlated jumps, consider the situation depicted in Fig. 1. This model was introduced in Ref. [9]. For instance, the particle may arrive at level 1 of site i from the left. The transition probability to level 2 at site $i-1$ and the transition probability to level 1 at site $i+1$ can be different. On the other hand, it is clear that the probability to jump forward or backward will be greatly affected if the arriving particle lands on levels 2 or 3. Although in the original work of Ref. [9] the model was studied from the point of view of a solitaire walker, it can be expected that the existence of internal states will affect the collective diffusion behavior in a many particles system. Then, the collective diffusion properties of simple 1d profiles deserve to be analyzed when correlations among jumps of individual particles are included.

This work is organized as follows. In Section 2, we present the model and the computational method used to determine the diffusion coefficient by using the BM approach. In Section 3, we analytically show, in a new and simple way, which is the value of the collective diffusion coefficient as a

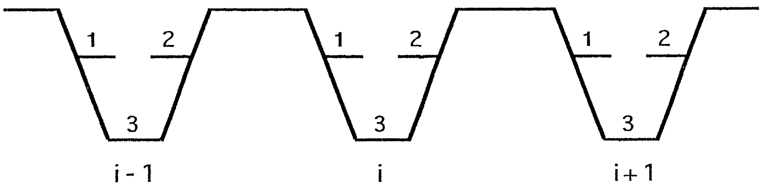

Fig. 1. One-dimensional scheme of a periodic potential with three energy states.

function of the amount of correlation of each particle, when there is no lattice gas restriction. By means of kinetic Monte Carlo simulations, in Section 4 we show that the value of the diffusion coefficient $D(c)$ is strongly influenced by the type and amount of correlation included. Also, we studied the combined effects of correlations and single occupancy restriction (lattice gas restriction). We show that when correlations are present, the lattice gas restriction strongly reflects on the resulting values of the diffusivity. The BM method was specifically chosen because it is the standard procedure used to measure the collective diffusion coefficient in experimental situations. Finally, in Section 5, conclusions are summarized.

2. Discrete model and computational method

By using a Monte Carlo kinetic scheme, the diffusion of a 1d profile is simulated. To determine the diffusion coefficient we will apply the BM method to the profile resulting from an initial step concentration after a fixed amount of time. Then, by means of Eq. (2) $D(c)$ will be calculated for the different cases discussed below. We will also present results for an initial stripe concentration profile because clearly shows the consequences of correlation on the profile evolution, although the BM method cannot be used in this case.

In the simulation, correlation is introduced as a 'memory' between jumps in the RW of each one of the individual particles. In the simple case adopted here, the selected direction of jumping depends on the direction of the previous jump. For the lattice gas approach, the 'surface' is modeled by a one-dimensional lattice with L sites. Each site of the lattice can take the value 1 or 0 indicating that the site is occupied by a particle or not. To setup an initial step concentration profile, at $t = 0$, the system is prepared in such way that sites in the range $-L/2 \leqslant i \leqslant 0$ are filled, where i is the discrete lattice site index. The rest of the lattice sites are set to 0. This is equivalent to consider a continuous case in which initially for $x < 0$ the concentration $C(x,0) = 1$, while the rest of the surface has an initial concentration $C(x,0) = 0$. Time in simulations is measured in terms of Monte Carlo steps (MCS), with one MCS defined as the time for a particle to be selected for jumping once on the average. As pointed above, we have also performed simulations for an initial stripe concentration profile in which sites in the range $-100 \leqslant i \leqslant 100$ are initially occupied.

For the 1d Langmuir model (LM), an ideal lattice gas model, each particle is considered to make a correlated RW, jumping left or right according to the following rules. When a particle is chosen at random, its previous step direction is taken from a register where the direction of the previous jump for each particle is maintained. Then, the present jump direction is selected to be the same of the previous one with probability q and to be opposite with probability $1 - q$. At $t = 0$, the register is filled with left or right jump directions selected at random with equal probability. If the selected site to jump to is filled no action takes place and the jump register for the selected particle is reset to equal backward and forward jump probabilities. This accounts for a thermalization effect, in which the particle losses its memory when it cannot make a jump. Note that if q is set to 0.5 the standard non-correlated RW behavior is recovered. For $q > 0.5$, the particle movement is considered to be persistent, making the particle trying to keep moving in the same previous direction (inertia effect). For $q < 0.5$, the movement is considered to be anti-persistent, the particle prefers to go in the opposite direction than that of the previous jump. Since we are dealing with a discrete model, interactions among particles can be easily included. However, interactions among particles are not considered here in order to make clear which are the effects of the correlations on the collective behavior. In order to simulate the continuous model (CM), a simulation that is equivalent to solving Eq. (1) is carried out by removing the single occupancy restriction, i.e. sites in the lattice can be occupied by any number of non-interacting particles.

3. Theory for the continuous model

The usual method to determine diffusion coefficients in regular lattices consists in establishing the appropriate master equations and then a Fourier expansion leads to an eigenvalue problem (for instance, see Ref. [7]). Eigenvalues are calculated and the diffusion coefficient can be determined. Here, we will show an alternative approach to determine diffusion coefficients, not regularly used in the literature, but which largely simplifies the calculations [10].

In principle, two different types of diffusion coefficients must be distinguished. The chemical or collective diffusion coefficient, defined by means of Fick's law in the presence of a macroscopic concentration gradient, and the tracer diffusion coefficient, defined in terms of a RW of a single particle [11]. In general, depending on the system under study, these definitions give rise to different values. However, if the collective diffusivity is figured out for the zero-coverage limit (which is equivalent to consider non-interacting particles) both definitions for diffusivity become the same. In our alternative approach, this equivalence is exploited.

In order to include correlations effects, the number of particles at a site i has to be split into two contributions, n_i^+ and n_i^-, where $+$ and $-$ indicate that the particle came from the site $i+1$ or $i-1$, respectively. We will consider three sites (arbitrarily labeled 0, 1, and 2), as depicted in Fig. 2. We assume that site 0 is an ideal sink for particles, i.e., $n_0 = 0$. Then, particle fluxes can be expressed as

$$\begin{aligned} J_0^+ &= 0, \\ J_1^- &= n_1^+ q = n_1 q, \\ J_1^+ &= n_1^+(1-q) = n_1(1-q), \\ J_2^- &= n_2^+ q + n_2^-(1-q), \end{aligned} \tag{4}$$

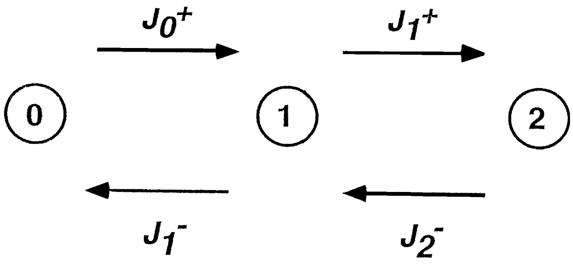

Fig. 2. Representation of three sites and fluxes associated.

where we have considered that $n_1^+ = n_1$ since $n_1^- = 0$.

Under steady-state conditions, the number of particles at a site must remain constant with time; then the following equations can be written:

$$\begin{aligned} \frac{dn_1^+}{dt} &= n_2^+ q + n_2^-(1-q) - n_1^+ = 0, \\ \frac{dn_2^-}{dt} &= n_1^+(1-q) - n_2^- = 0. \end{aligned} \tag{5}$$

With these equations n_2^+ and n_2^- can be expressed as a function of n_1 as

$$\begin{aligned} n_2^- &= n_1(1-q), \\ n_2^+ &= n_1(2-q). \end{aligned} \tag{6}$$

The total number of particles at site 2 can be easily calculated as $n_2^+ + n_2^-$ and then the difference between the number of particles at sites 2 and 1 is

$$n_2 - n_1 = 2n_1(1-q). \tag{7}$$

With Eq. (4), the net flux between sites 1 and 2 is calculated to be qn_1. Finally, using Ficks's first law, the diffusivity can be determined as

$$D = \frac{q}{2(1-q)}, \tag{8}$$

which is the same result obtained in Ref. [3] using the standard Fourier transform procedure. Although special boundary conditions were used, the same result for the diffusivity can be obtained assuming a non-zero number of particles in site 0. The present adopted boundary conditions lead to the simplest derivation.

4. Results and discussion

In order to qualitatively show the effects of correlations we present in Fig. 3 the profiles resulting from an initial stripe concentration after a certain amount of time. Profiles were collected at $t = 4000$ MCS with and without the single occupancy restriction and for three values of q; $q = 0.5$ (standard RW), $q = 0.8$ (persistent movement), and $q = 0.2$ (anti-persistent movement). All

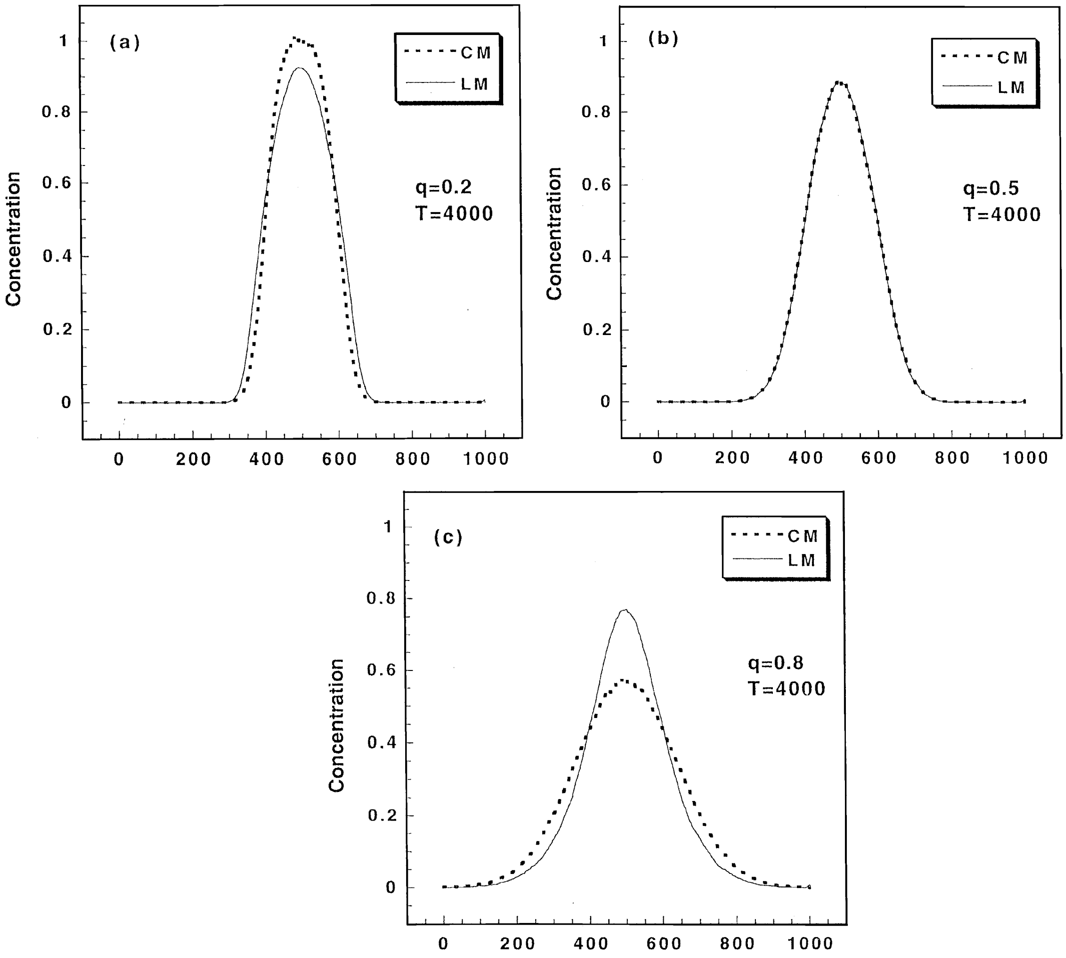

Fig. 3. Diffusion profiles for the CM and the lattice gas (LM) model corresponding to anti-persistent movement (a), a regular RW (b), and a persistent movement (c).

numerical results presented are averages over 3000 independent runs. Other profiles corresponding to different times were also collected but they display the same characteristics as the ones shown. It can be seen that for $q = 0.5$ the standard linear behavior is recovered and the lattice gas restriction has no influence at all. This means that the profile follows the normal shape of the solution obtained by solving the linear diffusion equation (Eq. (1)). On the other hand, it is apparent that the shape is not conserved for the persistent or anti-persistent cases. Also, it is clear that the lattice gas restriction originates very different profiles when the microscopic movement of the diffusing particles is correlated.

In order to calculate the diffusion coefficient as a function of concentration we applied the BM method to an initial step profile. Fig. 4 summarizes the resulting diffusivities $D(c)$ from the obtained profiles at $t = 4000$ MCS. Calculations were made for $q = 0.25$, 0.5, and 0.75. Results are normalized to the diffusivity for $q = 0.5$. The error involved in calculating the derivative needed to use Eq. (2) precludes the application of the BM method at very high or very low concentrations. Nevertheless, the obtained diffusivities for very low

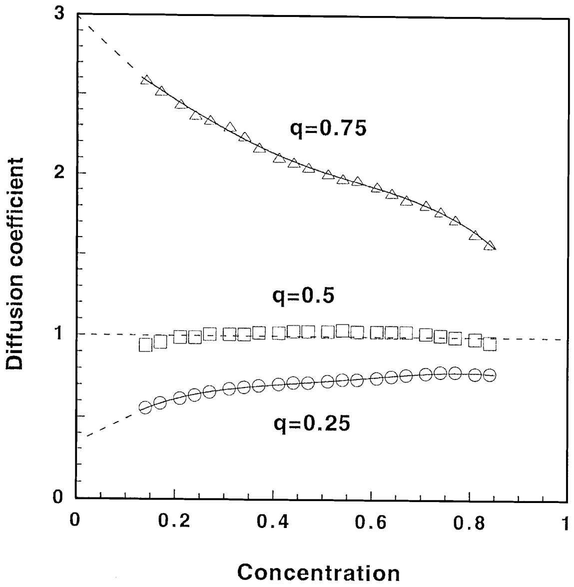

Fig. 4. Diffusion coefficient referred to $D(q = 0.5)$ as a function of concentration determined through the BM method with the lattice gas restriction for three values of the correlation parameter q.

concentrations indicate the tendencies toward the theoretical values obtained from Eq. (8). In the persistent case, particles seem to have a great chance to diffuse away from the original occupied site, giving the net result of a higher diffusivity. On the contrary, in the anti-persistent case particles would have less chance to jump away with the net result of a less diffusive collective behavior.

It can be seen that the restriction of single occupancy has very important effects. As already observed in Fig. 3 and directly quantified in Fig. 4, the diffusivity is significantly affected if correlations are also present. These results can be considered to be an effect of the excluded volume. Indeed, particles cannot always continue their movement forward in the persistent case because they interfere with other particles. Similarly, in the anti-persistent case not always particles can move backward as dictated by a low q because of the low probability of finding the appropriate site available. As a consequence, the diffusivity for the lattice gas model is smaller than that for the multiple occupancy model if $q > 0.5$ and larger if $q < 0.5$. These differences increase with concentration as it is clearly revealed in Fig. 4. Note that for $q = 0.5$ the same value of D is always determined, since this is the non-correlated case.

5. Conclusions

The collective effect of correlations on the microscopic movement of diffusion particles has been analyzed by means of kinetic Monte Carlo simulations for the diffusion of one-dimensional concentration profiles. The approach adopted here is a very simple one, making two successive jumps to be correlated (or anti-correlated). However, the results shown indicate that the combined effect of single occupancy and correlations is crucial for the resulting patterns evolution. Also, we present a new way to determine the value of the collective diffusion coefficient as a function of the amount of correlation of each particle, for multiple occupancy condition. When the lattice gas condition is present, the value of diffusivity becomes dependent on the concentration and then when applying the BM method, the measured value is a function of the specific point of the profile where the measurement is done. Note that these results show a coverage dependent diffusivity despite the absence of interactions among particles. It is known that, in some realistic experimental situations, particle jumps may be correlated with more than a single previous step. In that case, it is expected that the collective behavior will be affected in a more complicated manner.

Acknowledgements

This work was partially supported by the National Council for Scientific and Technical Research (CONICET) of Argentina.

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