Combined effect of periodic gates and external fields on the diffusion coefficient of a single particle

Lida Oum,[1] Juan M. R. Parrondo,[2] and Hernan L. Martinez[1,*]
[1]*Department of Chemistry, California State University, Dominguez Hills, Carson, California 90747*
[2]*Departamento de Física Atómica, Molecular y Nuclear, Universidad Complutense, 28040 Madrid, Spain*
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A general analytical expression to describe the diffusion of a single particle in a one-dimensional lattice with periodically distributed gates of lifetime (τ) and while under the influence of a constant external field is calculated. A formulation based on a microscopic model and a diffusion relaxation condition is used to derive an equation for the diffusion coefficient as a function of the concentration of gates (c), the lifetime (τ) of such gates, and the strength of the external field (p). The theory is compared against Monte Carlo simulations, and limiting cases are used to reproduce previously published results on a variety of phenomena.

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I. INTRODUCTION

The subject of diffusion within different types of media has been the focus of increasing interest over the past few decades [1,2]. Diffusion plays an essential role in a wide variety of physical and chemical phenomena involving chemical kinetics [3], conductivity [4], glasses [5], cellular media [6,7], etc. A considerable amount of work has been devoted to the study of diffusion in disordered media. In particular, it has been observed that transport properties are highly sensitive to structural changes. However, a complete description of all possible interactions between diffusion and such disorder remains an active area of research, where new phenomena are discovered regularly. In order to study diffusion in disordered media, fractal structures have often been used to represent geometrical disorder [8,9]. An energetic disorder has also been introduced, but mainly in the form of the dichotomic [10] and the Ehrlich-Shwoebel [11,12] barrier models. Anomalous diffusion has been observed in all the aforementioned cases. The presence of a bias, which also affects a particle's motion, provides an additional variable to an already complex phenomenon in both geometrically [9] and energetically [13,14] disordered lattices.

Cellular media have been identified with multiple materials ranging from biological tissues to soap suds. These media consist of consecutive finite cells separated by permeable walls. Each cell consists of energy potential wells separated by energy barriers, all of equal magnitude. The linear size of a cell is determined by the number of these potential wells, all of which are available for a particle to visit. According to the dichotomic barrier model, larger energy barriers surround each cell and act as walls of reduced permeability. In order to study diffusion in this periodic array of small and large barriers, the jump probability to overcome the larger barriers is different from that of the smaller barriers. In an alternative description of this medium, the barriers are replaced by traps characterized by specific mean stay times [7]. Step motion on crystal surfaces can also be studied in terms of a periodic distribution of potential wells and barriers. The main difference is that the edges of the stepped surface not only involve different potential barriers, but also different potential wells [12,15]. These systems were studied in terms of temperature and its effect on the particle's diffusion.

The purpose of this paper is to study the diffusion coefficient of a single particle moving along a simple geometrical representation of cellular media while under the influence of a constant external field. We use a statistical microscopic model of a biased random walk to study this phenomenon. We obtain a general equation which describes our system as well as other systems previously reported in the literature. In particular, we draw connections between our model and those previously used to represent diffusion on a stepped surface [15], cellular media [6,7], and simple biased diffusion. We also relate our results to a system that was proposed to mimic properties of glass transition [5]. The geometrical characteristics of the latter inspired the lattice model used herein. Our system is nonthermal, and the interaction between particle and gates is strictly steric.

This paper is organized as follows. Section II describes the model used as well as the mathematical details of our calculation. Section III compares our analytical results to our system's Monte Carlo simulations. Section IV illustrates how limiting cases of our calculations reproduce known results for other systems.

II. MODEL AND CALCULATIONS

We consider the diffusion of a single particle along a one-dimensional discrete lattice. The lattice consists of an infinite series of consecutive cells where each cell contains the same number of lattice sites. Gates are placed between two lattice sites to separate two consecutive cells from each other. The main feature of this model is that these gates have a dimensionless lifetime τ, after which they all disappear simultaneously during one-particle's jump. All then reappear in the same place during the next τ jump attempts. In other words, since the gates are removed every τ units of time only to return one unit of time later then τ represents the lifetime of a cell. As can be deduced, τ is directly related to what in cellular media is known as the permeability of the wall. The particle diffuses along this system under the influence of a constant external field. Figure 1 describes the system.

*Author to whom correspondence should be addressed; electronic address: leoh@cali.csudh.edu

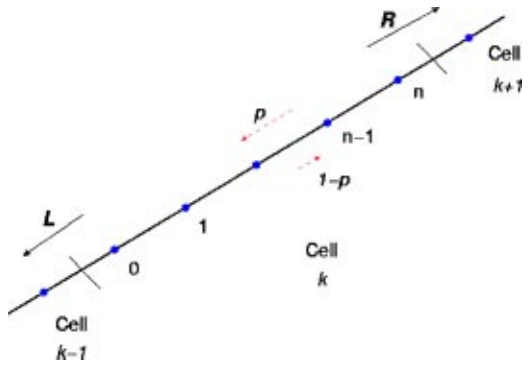

FIG. 1. (Color online only) This schematic representation of the model shows a cell consisting of $n+1$ sites, enumerated from zero to n. The cell is surrounded by two other cells of the same size. p and $1-p$ are the microscopic jumping probabilities for a particle to move to its nearest neighbors. R and L are the probabilities of escaping the cell.

Our model is similar to one proposed by Ivanov *et al.* to mimic certain properties of glass transition [5]. In their model, the gates were not all synchronized to appear and disappear at the same time.

Our procedure first assumes diffusion relaxation in a cell in order to calculate a site's occupation probability. It enables us to calculate the probability of the particle escaping a cell both to the right (R) and to the left (L). These probabilities are then used to calculate the first and second moments of the distribution and the corresponding dispersion for the particle's motion from cell to cell. The expression obtained for such dispersion is then compared to the well-known result $\langle x^2(t)\rangle-\langle x(t)\rangle^2=2Dt$. This comparison allows us to derive an analytical equation for the diffusion coefficient in terms of the size of the cell, the lifetime periodicity of the cell (τ), and the strength of the field (which in our analysis is given in terms of the probability of motion p). The physical assumption of diffusion relaxation implies an intrinsic mathematical relationship between the lifetime of a cell and its size. This fact becomes evident in the mathematical description given below.

In order to calculate the diffusion coefficient for this process, we must find an expression for the dispersion of a particle jumping between cells. This implies the need to calculate the first and second moments of that distribution. Using Γ as the jumping frequency ($1/t'$, where t' is the time for each hopping attempt) and $l_{\mathrm{cell}}=(n+1)l_o$ as the size of a cell [we define l_o as the distance between two lattice sites and $(n+1)$ as the number of sites per cell], the equations for those moments are

$$\langle x(t)\rangle=\frac{tl_{\mathrm{cell}}\Gamma}{\tau}(R-L), \tag{1}$$

$$\langle x^2(t)\rangle=\frac{tl_{\mathrm{cell}}^2\Gamma}{\tau}(R+L). \tag{2}$$

The dispersion for our system can now be calculated using Eqs. (1) and (2)

$$\langle x^2(t)\rangle-\langle x(t)\rangle^2=\frac{tl_{\mathrm{cell}}^2\Gamma}{\tau}[(R+L+2RL-R^2-L^2)]. \tag{3}$$

We now compare Eq. (3) to the known equation for the dispersion, $\langle x^2(t)\rangle-\langle x(t)\rangle^2=2Dt$, to obtain the following equation for the diffusion coefficient:

$$D=\frac{(n+1)^2D_o}{\tau}(R+L+2RL-R^2-L^2), \tag{4}$$

where $D_o=\Gamma l_o^2/2$ corresponds to the normal diffusion constant. This is the most general expression for the diffusion coefficient in this system.

Since our concern is to find an explicit relationship between the diffusion coefficient D and the system's variables p, c, and τ, we must calculate the escaping probabilities R and L in terms of those variables. The probability for the particle to jump from $i\rightarrow(i+1)$ is $(1-p)$, while the probability of jumping from $(i+1)\rightarrow i$ is p in a cell containing $(n+1)$ sites (the sites in the cell are numbered from 0 to n), as shown in Fig. 1. According to the principle of detailed balance [16], the following hierarchy of equations must be satisfied by the stationary distribution:

$$\begin{aligned} P_o(1-p)&=P_1p,\\ P_1(1-p)&=P_2p,\\ &\vdots \end{aligned} \tag{5}$$

whose general solution is

$$P_i=\alpha^iP_o \tag{6}$$

with $\alpha=(1-p)/p$. Imposing the normalization condition for the probability distribution within the cell, $\Sigma_{i=0}^{n}P_i=1$, we find

$$P_n=\left(\frac{1-\alpha}{1-\alpha^{n+1}}\right)\alpha^n, \tag{7}$$

where we have assumed $\alpha<1$ (i.e., $1/2<p\leqslant 1$), which represents the intrinsic presence of a field. The specific case of $\alpha=1$ or $p=1/2$ will be discussed in Sec. IV C.

The distribution given by Eq. (7) is the stationary distribution within the cell. As mentioned before, we will assume that the gates are closed for a period of time long enough to reach this stationary distribution. With this assumption, the probability of a particle escaping a given cell so that it can move to either the cell's right $[R=P_n(1-p)]$ or left $(L=P_op)$ can now be calculated

$$\begin{aligned} R&=\left(\frac{1-\alpha}{1-\alpha^{n+1}}\right)\alpha^n(1-p),\\ L&=\left(\frac{1-\alpha}{1-\alpha^{n+1}}\right)p. \end{aligned} \tag{8}$$

Using these equations for R and L in our general expression for the diffusion coefficient [Eq. (4)], we obtain

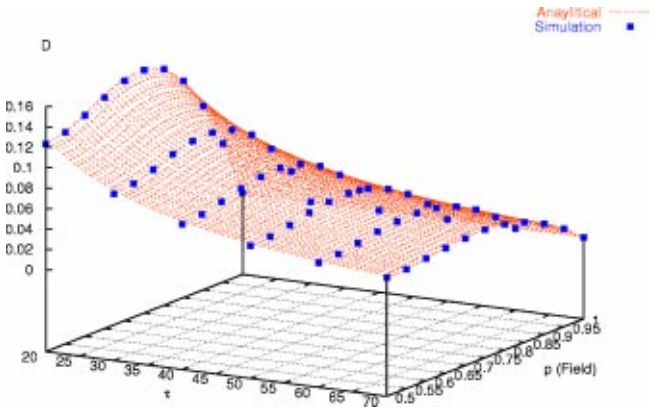

FIG. 2. (Color) Comparison between analytical results using Eq. (10) (continuous mesh) and Monte Carlo simulations (dots). We have plotted $D(c,\tau,p)$ vs τ vs p (field's strength), including the case $p=1/2$, which is discussed in Sec. IV C. The concentration of gates is $c=0.2$. The quantities c, τ, and p are dimensionless. D has units of $D_o(l_o^2\Gamma)$.

$$D(n,\tau,p)=\frac{2(n+1)^2D_o}{\tau}\frac{\left[1+\left(\frac{1}{p}-1\right)^n\right](2p-1)(1-p)p}{\left(\frac{1}{p}-1\right)^n(p-1)+p}. \tag{9}$$

Furthermore, since the cells are all of equivalent size $(n+1)$, the dimensionless concentration of gates is given by $c=1/(n+1)$. Substituting in Eq. (9), we obtain

$$D(c,\tau,p)=\frac{2D_o}{c^2\tau}\frac{\left[1+\left(\frac{1}{p}-1\right)^{(1-c)/c}\right](2p-1)(1-p)p}{\left(\frac{1}{p}-1\right)^{(1-c)/c}(p-1)+p}. \tag{10}$$

Equation (10) is the general expression that describes the diffusion coefficient for our system (D), but is now given in terms of: the concentration of gates (c), the period of time during which the gates remain closed (τ), and the field strength (as measured by p).

III. ANALYTICAL RESULTS AND SIMULATIONS

To ascertain the validity of our analysis, we compare our analytical results from Eq. (10) against Monte Carlo simulations of the one-dimensional system discussed herein. The Monte Carlo simulations consist of a single particle that is allowed to jump to either of its nearest neighbor sites, provided not a standing gate obstructs the path. If a standing gate is present, the particle remains at the site for that unit of time. Each trajectory consists of 3×10^4 units of time and is characterized by a given value of c, τ, and p. A total of 10^5 trajectories for each selection of c, τ, and p are explored. Periodic boundary conditions are used to simulate an infinite lattice.

Figure 2 shows an excellent agreement between our analytical prediction and the Monte Carlo simulation for the case when the concentration of gates is $c=0.2$.

It is important to notice the shape of the surface describing the diffusion coefficient in terms of the hopping probability p and the lifetime of the cells τ. We notice that for any given value of c and p, the diffusion coefficient decreases as the lifetime of the cell increases. This can readily be derived from Eq. (10) by taking the partial derivative of $D(c,\tau,p)$ with respect to τ, and by realizing that the resulting expression will be always negative and proportional to $-\tau^{-2}$. This also implies that the value of the diffusion coefficient changes more dramatically in the presence of short-lived cells and stabilizes as the cells become long lived. A generally similar situation can be predicted from Eq. (10) for the dependence of $D(c,\tau,p)$ with respect to c. The diffusion coefficient decreases as the concentration of gates increases (or the size of the cell decreases).

Additionally, we observe the presence of a maximum on the $D(c,\tau,p)$ vs p plane. This is more clearly seen in Fig. 3, which shows the diffusion coefficient in terms of the hopping probability. Noticeably, for certain τ and c, increasing the strength of the field enhances the particle's diffusion up to a given field strength. The effect of increasing the strength of the field is contrary after that point to the extent that no diffusion is observed at very strong fields $(p=1)$; the walk becomes completely deterministic.

Also, we notice that for a given value of τ, the accuracy of the match between theory and simulations is affected as gate concentration decreases. This occurs because our assumption of diffusional relaxation within a cell is not met under these circumstances. The particle does not have enough time to visit all sites of a given cell before the gates open. It is apparent from this observation that τ and c are intimately related to guarantee diffusional relaxation within a cell. We have observed that a strong agreement is found whenever the product $\tau c \gtrsim 4$. As that product becomes smaller, the theoretical calculation deviates mainly for the small fields, as the particle performs a less deterministic walk.

IV. SOME LIMITING CASES

A. Biased diffusion with waiting time

Diffusion with waiting time can be represented by a particle jumping to its neighboring sites and remaining stationary for some time before attempting another jump. The motion of this "sticky" particle can be achieved in our model by filling the lattice with gates. Since gates are placed between lattice sites in our system, when $c=1$, there is always a gate between two lattice sites. The particle is then forced to remain at that site for τ units of time until the gates open. At that time, the particle jumps to one of its nearest lattice sites. The equation that describes this process is derived from Eq. (10) when gate concentration is set at $c=1$. Our equation becomes

$$D(\tau,p)=\frac{4D_o}{\tau}(1-p)p. \tag{11}$$

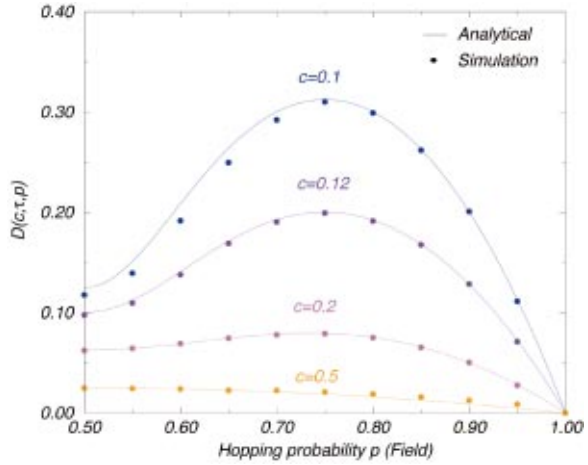

FIG. 3. (Color online only) Analytical results and Monte Carlo simulations for $D(c,\tau,p)$ vs p, for $\tau=40$ at different gate concentrations and using the same units as in Fig. 2. The line corresponding to $c=0.2$ is a slice of Fig. 2.

The calculation becomes exact in this limit because the relaxation condition is always met as it only takes one unit of time to visit that one site in the cell. This is confirmed by Fig. 4, where we have plotted $D(\tau,p)$ vs p. Notice the exact agreement between the analytical result [Eq. (11)] and the Monte Carlo simulations.

B. Simple biased diffusion

Biased diffusion in a lattice free of obstacles can also be represented in our model by saturating the lattice with gates ($c=1$), provided that $\tau=1$. In other words, the gates are forced to open every time the particle attempts to jump; essentially there is an absence of barriers. This scenario, which is not considered a cellular medium, cannot be represented directly by our model (i.e., for $c=0$).

Adding the condition $\tau=1$ to Eq. (11), a known equation [17] that describes simple biased diffusion can be derived,

$$D(p)=4D_o(1-p)p. \tag{12}$$

Results from Eq. (12) and its corresponding simulation results are shown in Fig. 4 under the label $\tau=1$.

C. Unbiased diffusion on a simple model of cellular media

The typical model of cellular media involves the unbiased motion of a particle in a cellular lattice [6,7]. We can calculate the diffusion coefficient by taking the limit $p\to 1/2$ in Eq. (10) or, more simply, by recalculating the escaping probabilities R and L, which now read

$$W=L=R=\frac{1}{2(n+1)} \tag{13}$$

and use them in Eq. (4). The final result is

$$D=\frac{2W(n+1)^2D_o}{\tau}=\frac{D_o}{c\tau}. \tag{14}$$

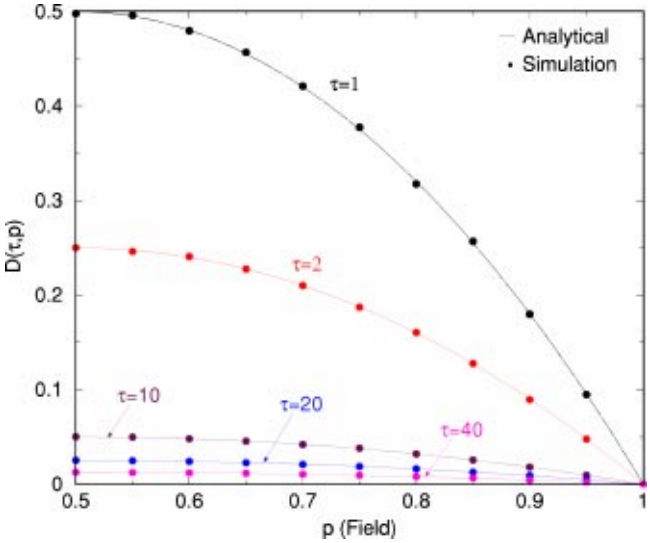

FIG. 4. (Color online only) Analytical results vs simulation for a biased random walk. The calculation becomes exact in this limit as seen in the perfect fit between the analytical prediction and the Monte Carlo results. Units are the same as in Fig. 2.

Equation (14) agrees with several results previously reported in the literature; those studies used different methods for unbiased diffusion in similar types of media. Here we relate Eq. (14) to some of those results.

Milchev *et al.* studied the problem of a particle diffusing in a dichotomic barrier model [6]. Their study focused on different diffusion regimes arising from the model. Their formulation allowed them to find a proportionality relation for the diffusion coefficient as ($t\to\infty$): $D_\infty\approx pL$, for $pL\ll 1$. L was defined as the size of the cell and p as the jump rate to overcome the higher barriers (so that we can identify p as being proportional to τ^{-1}). As can be seen, Eq. (14) correctly describes the long-time behavior predicted in that paper.

Natori and Godby studied surface diffusion on a stepped surface [15]. An analysis similar to tight-binding theory of electronic structure yielded expressions for the diffusion coefficient in both the x and y directions. The x direction in that model resembled a ladder where the particle is free to move. Different jumping rates were defined depending on whether the particle was moving on a step of the ladder or trying to move up or down to the next step. When we modify those rates to coincide with our model (i.e., rates within the step equal to each other, and the rate to go up a step equals to the rate for going down $\Gamma=\Gamma_1$), we can compare their results to Eq. (14). We do so by realizing that the Schwoebel and Shipsey factor (S) [12] is proportional to τ^{-1}, and by identifying $c=1/n$ (using their labeling notation). For the case in which $S\to 0(\tau\to\infty)$, their diffusion coefficient result becomes $D=D_oSn$, which is the same as our Eq. (14).

Ivanov *et al.* proposed several one-particle, purely diffusional models to mimic specific properties of glass transition [5]. The model we study in this paper (Fig. 1) is based on their model *A*. Their model consisted of a lattice with equally distributed barriers which would open after τ units of time. However, the barriers did not open in a synchronized man-

ner. Instead, the starting point of a sequence was chosen at random for *each* particle. Also, their study was specific for simple diffusion and did not include the influence of a bias. They pointed out in their paper that slight changes in the lattice model could lead to drastic changes in the diffusion. As expected, the expression for the diffusion coefficient they obtained for model *A* differs from our result. However, it is important to notice that in the limit when the product τc becomes large, both their expression and our Eq. (14) decrease as $(\tau c)^{-1}$.

V. CONCLUSIONS

We have derived a general equation, Eq. (4), which describes the diffusion coefficient of a single moving particle while confined to a medium with equal size cells of lifetime τ and under the influence of an external field. The only assumption in this derivation is the lifetime τ of the cells to be long enough to allow diffusional relaxation within them. For zero fields, this means τ must be much longer than the square of the size of the cell $(n+1)^2=1/c^2$, i.e., $\tau c^2 \ll 1$. On the other hand, if the field is present, the relaxation of time grows linearly with $(n+1)$. By extensive simulations of the system, we conclude that our assumption is fulfilled whenever $\tau c \gtrsim 4$ for small fields.

Equation (4) encompasses features of this system that have so far been discussed separately in the literature such as cellular media, surface diffusion on stepped surfaces, glass transition, ion channel permeation, etc. We have captured the most important features affecting the diffusion coefficient in these types of media using a very simple lattice model and a general nonthermal mathematical formulation. We are also able to use our formulation to describe situations in which the system has no gates. Interestingly, we do so by realizing that our model is equivalent to such cases when $c=1$. Our formulation successfully describes a biased walk with waiting times Eq. (11) and a simple biased random walk Eq. (12). Finally, we can describe the process of a single particle moving in our model without the influence of an external bias using Eq. (14). All these findings agree with previously published results covering numerous phenomena.

Our model also shows and explains new features which have not yet been observed. In particular, we observe that, for a given concentration of gates, either a strong field or a weak field may have the same effect on the diffusion of the particle. An optimal combination of field and gate concentration provides maximum diffusion. This was observed in the $D(c,\tau,p)$ vs p plane (Fig. 3). We are not aware of this dependency being discussed in the literature. Instead, in previous studies of a biased random walk in energetically disordered lattices, Monte Carlo techniques have been used to study the mean-square displacement and its dependency on the temperature of the system, as well as the effect of an alternating field [14]. Also, the currents produced by a strong bias have been studied using detailed balance [18].

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