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Building reliable lattice Monte Carlo models for real drift and diffusion problems

Michel G. Gauthier* and Gary W. Slater†
Department of Physics, University of Ottawa, 150 Louis-Pasteur, Ottawa, Ontario, Canada K1N 6N5
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We revisit the well-known issue of representing an overdamped drift-and-diffusion system by an equivalent lattice random-walk model. We demonstrate that commonly used Monte Carlo algorithms do not conserve the diffusion coefficient when a driving field of arbitrary amplitude is present, and that such algorithms would actually require fluctuating jumping times and one clock per Cartesian direction to work properly. Although it is in principle possible to construct valid algorithms with fixed time steps, we show that no such algorithm can be used in more than two dimensions if the jumps are made along only one axis at each time step.

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Diffusion plays a key role in numerous physical, chemical, and biological systems [1]. When an analytical solution to the diffusion equation cannot be obtained, it is common to replace an overdamped continuous diffusion problem by Monte Carlo (MC) simulations of the random walk of a particle on a lattice. We recently derived a mathematical method that provides the exact solution of the standard lattice Monte Carlo (LMC) algorithm rewritten as coupled Master equations [2]. The method actually calculates the exact mobility μ of the random walker when a vanishing external force ($F \to 0$) is applied; the Nernst-Einstein relation between the diffusion coefficient D and μ then yields D even in the presence of obstacles and complicated boundary conditions. It is important to note, however, that the Nernst-Einstein relation is only valid in the $F \to 0$ limit. Another exact method was also suggested by Dorfman [3].

More recently [4], we developed a generalized LMC algorithm, and the corresponding exact calculation method, in order to compute field-dependent mobilities $\mu(F)$ for arbitrary values of F. However, as we will discuss below, $D(F)$ is quite subtle. In fact, it is astonishing to note that, although hundreds of LMC studies have been published over the years, none of these recover the right diffusion coefficient for a free particle under the influence of a strong bias. Standard algorithms are effectively limited to small forces F; e.g., this is the case for the popular repton model of gel electrophoresis [5] and for a recent study of diffusion effects in a microfluidic device [6]. In many studies of diffusion in porous systems, however, the chosen LMC algorithm is in fact quite generic, because the authors are not trying to map a real diffusion system onto a lattice random-walk problem; in such cases, the time scale is generally not field dependent and it is not clear how the quantitative results can be interpreted in terms of real physical systems. In other cases, the simulation results are apparently limited to small biases, although it is not always explicitly mentioned (see, e.g., [[7–10]]). For instance, one can look at the problem of the *survival* probability of a biased random walker in a disordered medium [11,12]. Biased random walks can also be studied in the context of continuous time random walks (CTRW) [13,14]. Again, CTRW articles appear to be restricted to small biases. In this article, we will only consider discrete time random-walks.

Drift in one dimension (1D). Our objective is to derive a valid LMC model that reproduces the mean dynamical properties of a Brownian particle moving in a fluid under the influence of an external force F. For instance, it must recover, in the overdamped limit (no acceleration and no turbulence), the free-solution velocity $v_0 = F/\xi_0$ and the field-independent diffusion coefficient $D_0 = k_B T/\xi_0$, where ξ_0 is the particle's friction coefficient, k_B is Boltzmann's constant, and T is the temperature [15]. In order to use LMC algorithms to study the migration of (pointlike) particles in continuous space, we first discretize space. In 1D, the continuous motion of the particle is replaced by a series of discrete jumps between sites separated by a distance a. Let $p_\pm$ be the probabilities for a particle to move to the two adjacent sites ($+$ and $-$) and τ be the time duration of such a jump. Completion of a jump is similar to a first-passage problem between two absorbing walls, as shown in Fig. 1. If $F=0$, the probabilities $p_\pm = \frac{1}{2}$ are unbiased and the mean time duration τ_B of a jump (also called the Brownian time or the mean first-passage time) is related to D_0 via $\tau_B = a^2/2D_0$. When $F>0$, however, the transition probabilities are biased and the jumps take less time [$\tau(F) < \tau_B$]. Fortunately, exact analytical ex-

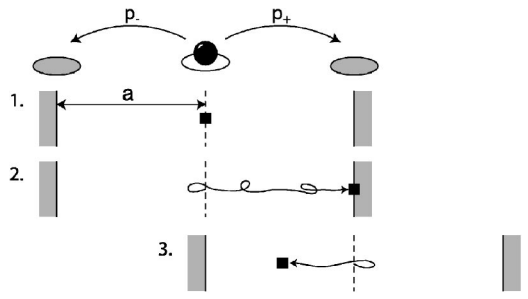

FIG. 1. Brownian particle diffusing between two absorbing walls. The values of $\tau(\epsilon)$ and $p_\pm(\epsilon)$ can be obtained either exactly or numerically. In the latter case, the simulation steps are (1) placing the particle at a distance a from each wall, (2) letting it diffuse, via Brownian dynamics, until it reaches a wall, and (3) restarting the process from the new site.

*Email address: mgauthie@science.uottawa.ca
†Email address: gslater@science.uottawa.ca

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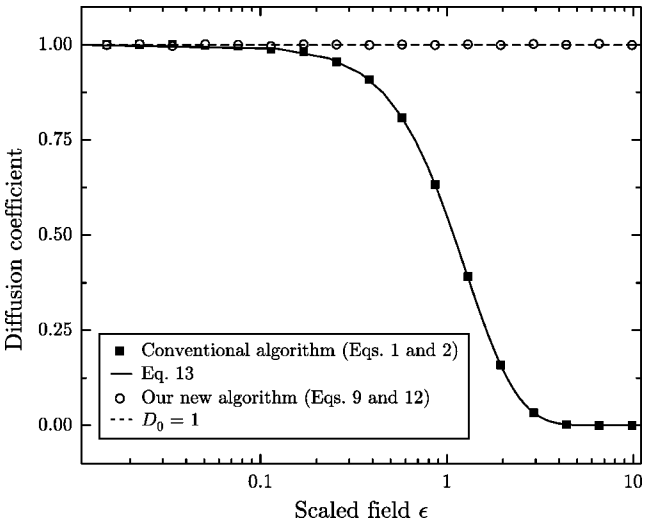

FIG. 2. Free-solution diffusion coefficient D_0 (in units of $a^2/2\tau_B$) vs the scaled field ϵ. The points were obtained from Monte Carlo simulations of 1 000 000 particles evolving on a square lattice. Error bars are smaller than the points.

pressions can be obtained for this first-passage problem [16–18] (see Fig. 1). The relevant variable here is the scaled external force $\epsilon = Fa/2k_BT$. At each step, the particle moves to one of the two neighboring sites (denoted + and − for parallel and antiparallel to the force F, respectively) following the probabilities [19]

$$p_{\pm}(\epsilon) = \frac{1}{1 + e^{\mp 2\epsilon}}, \tag{1}$$

while the mean time duration of each jump is [19]

$$\tau(\epsilon) = \frac{\tanh \epsilon}{\epsilon}\tau_B. \tag{2}$$

Remarkably, the transition time τ is the same for both directions. In fact, τ is the duration of a successful MC jump in a given direction ($\pm$), and not the mean time between successful jumps in a fixed direction. The mean free-solution velocity is then

$$v_0 = \frac{(p_+ - p_-)a}{\tau} = \frac{\epsilon a}{\tau_B} = \frac{Fa^2}{2k_BT}\frac{2D_0}{a^2} = \frac{F}{\xi_0}, \tag{3}$$

as it should be for an overdamped system [15]. The free-solution diffusion coefficient D_0 can be obtained from the variance $\langle \Delta x^2 \rangle$ of the displacement during a time step τ and the jump probabilities $p_{\pm}$ via the first $[\langle x \rangle = a(p_+ - p_-)]$ and second $[\langle x^2 \rangle = a^2(p_+ + p_-)]$ moments,

$$D_0 = \frac{\langle \Delta x^2 \rangle}{2\tau} = \frac{\langle x^2 \rangle - \langle x \rangle^2}{2\tau} = \frac{a^2}{2\tau_B}\left(\frac{\epsilon}{\sinh \epsilon \cosh \epsilon}\right). \tag{4}$$

However, since D_0 characterizes the spreading of the particles around their mean position, it cannot depend on F [while the velocity must increase linearly with F, as shown by Eq. (3)]. Therefore, Eq. (4) is clearly incorrect when $\epsilon \neq 0$ (see also, Fig. 2). This demonstrates that, even without collisions with obstacles, simple LMC algorithms fail to properly model diffusion in the presence of a net drift. In fact, it is *not* possible to derive a time step $\tau(\epsilon)$ and probabilities $p_{\pm}(\epsilon)$ that generate the proper free flow velocity v_0 and diffusion coefficient D_0 simultaneously.

Time-step fluctuations in 1D. This failure is due to the fact that Eq. (4) only considers the spatial fluctuations $\langle \Delta x^2 \rangle$ of the particles' biased Brownian motion. However, a second source of diffusion has to be considered if $\epsilon \neq 0$: the fluctuations in the time duration τ of a jump. In the presence of a bias, both types of fluctuations have to be considered in the calculation of the diffusion coefficient [19,20]

$$D_0 = \frac{\langle \Delta x^2 \rangle}{2\tau} + \frac{v_0^2 \langle \Delta \tau^2 \rangle}{2\tau}. \tag{5}$$

The variance of the jumping time, $\langle \Delta \tau^2 \rangle$, can also be calculated for the 1D first-passage problem [19],

$$\langle \Delta \tau^2 \rangle = \frac{\tanh \epsilon - \epsilon \operatorname{sech}^2 \epsilon}{\epsilon^3}\tau_B^2. \tag{6}$$

The second term of Eq. (5) then reduces to

$$\frac{v_0^2 \langle \Delta \tau^2 \rangle}{2\tau} = \frac{a^2}{2\tau_B}\left(1 - \frac{\epsilon}{\sinh \epsilon \cosh \epsilon}\right). \tag{7}$$

Clearly, adding Eqs. (4) and (7), as suggested by Eq. (5), gives $D_0 = a^2/2\tau_B$, which agrees with the continuum result [15],

$$D_0 = \frac{a^2}{2\tau_B} = \frac{\epsilon a}{\tau_B}\frac{k_BT}{F} = \frac{v_0 k_BT}{F} = \frac{k_BT}{\xi_0}. \tag{8}$$

Therefore, a fluctuating jumping time τ is essential if a LMC model (or algorithm) is to be used to study the diffusion of particles in the presence of a drift. This is the reason why all fixed time step MC algorithms fail at high field. We can introduce these temporal fluctuations using any distribution function that has the right mean value and variance [Eqs. (2) and (6)]. In a simulation, this condition can be easily satisfied by changing the fixed time step τ by the random increment $\tau \pm \sqrt{\langle \Delta \tau^2 \rangle}$ (with a randomly chosen sign). The well-known problem of enhanced diffusion in porous media can also be solved using Eq. (5) [20]; in such cases, the effect is due to the retardation of the particles that collide with obstacles during their net drift. We showed that even without such collisions, one must take into account the natural fluctuations of the mean-first passage times of the lattice jumps, since these jumps are like pseudocollisions introduced by the process of mapping a continuous process onto a discrete lattice. This seems to have been largely overlooked in the field.

Time-step fluctuations in $d \geqslant -2D$. This fluctuating one-dimensional LMC algorithm can be generalized to multidimensional simulations. This can be done in various ways, but we suggest the following algorithm for each step (or jump). (1) First, an axis is selected with a probability inversely proportional to the mean jumping time along this axis. Since the field ϵ must be along a Cartesian axis, this time is given by $\tau(\epsilon) \leqslant \tau_B$ along $\hat{\epsilon}$, and by τ_B along all other directions. In other words, the faster the process is along a particular axis,

the more often this dimension is selected. (2) The actual jump is then selected using Eq. (1) (where $\epsilon=0$ if the jump is $\perp\hat{\epsilon}$). As usual, if the destination site is an obstacle, the particle simply remains on the same lattice site. (3) Finally, in order to recover the proper diffusion coefficient along the field axis, the clock advances by the random increment $\tau\pm\sqrt{\langle\Delta\tau^2\rangle}$ *only* when the jump was made along $\hat{\epsilon}$. Note that since the second term of Eq. (5) is zero in the other directions, we do not really need clocks for transverse jumps; indeed, the $\hat{\epsilon}$ clock provides the proper mean elapsed time t for *all* directions. The diffusion coefficient in direction i (including $i=\hat{\epsilon}$) is then obtained using the simple relation $D_i=\langle\Delta r_i^2\rangle/2t$.

An algorithm with constant time steps in 1*D*. As we demonstrated above, time fluctuations must be part of a LMC simulation if $\epsilon\neq 0$. However, exact numerical techniques [3,4] require a fixed time step to allow us to solve the LMC algorithm exactly. A constant time step can also simplify MC simulations. We now show how temporal fluctuations can be introduced without changing the time increment: we simply add a probability to remain on the same lattice site at each MC step. Usually, an LMC particle must make one jump at each time step. Let us now introduce a probability s' for the particle to remain immobile. The new transition probabilities $p'_\pm$ and time duration τ' are given by

$$p'_\pm=(1-s')p_\pm,\quad \tau'=(1-s')\tau. \tag{9}$$

Both quantities must be rescaled by the same factor in order to conserve the value of the free-solution velocity v_0. Then, at each time step of fixed duration τ', the particle either jumps to one of the $\pm$ sites (with probabilities $p'_\pm$) or stays on the same site with probability s'. The idea here is to use the probability s' as a free parameter that we fix, such that we obtain the desired variance for the average *real* jumping time. The average periods of time $\langle\tau\rangle$ and $\langle\tau^2\rangle$ between two successful jumps are

$$\langle\tau\rangle=(1-s')\tau'\sum_{i=1}^{\infty} is'^{i-1}=\frac{\tau'}{1-s'}=\tau, \tag{10}$$

$$\langle\tau^2\rangle=(1-s')\tau'^2\sum_{i=1}^{\infty} i^2s'^{i-1}=(1+s')\tau^2. \tag{11}$$

Using Eqs. (2), (6), (10), and (11), the required probability s' is

$$s'=\frac{\langle\tau^2\rangle-\langle\tau\rangle^2}{\langle\tau\rangle^2}=\frac{\langle\Delta\tau^2\rangle}{\tau^2}=\frac{\coth\epsilon}{\epsilon}-\operatorname{csch}^2\epsilon. \tag{12}$$

We can now evaluate the free-solution diffusion coefficient D_0 using only the spatial part of Eq. (5) (first term),

$$D_0=\frac{a^2}{2\tau'}[p'_+ + p'_- - (p'_+ - p'_-)^2]=\frac{a^2}{2\tau_B}. \tag{13}$$

Note that we used $\langle\Delta x^2\rangle'=\langle x^2\rangle'-\langle x\rangle'^2$, $\langle x^2\rangle'=a^2(p'_+ + p'_-)$, and $\langle x\rangle'=a(p'_+ - p'_-)$. Using implicit time fluctuations through the probability s' allows us to obtain the correct result [Eq. (8)] without relying on explicit fluctuations and the second term of Eq. (5). Figure 2 compares conventional MC-biased random walks [Eqs. (1) and (2)] and our new algorithm [Eqs. (9) and (12)].

Using Eqs. (9) and (12), one can design reliable LMC algorithms with fixed time steps. Please remark that the probability to stay put [Eq. (12)] is the *only* solution that gives the correct results for both v_0 and D_0 for arbitrary values of ϵ when we want the ratio p_+/p_- to be consistent with Boltzmann statistics. Therefore, no valid fixed-time LMC algorithm exists with $s'=0$. The idea of waiting time in a random walk was also introduced by Montroll and Weiss [13] in the context of CTRW.

An algorithm with constant time steps in $d\geqslant 2D$. In a recent article [4], we showed how to use Eqs. (1) and (2) to obtain the exact field-dependent velocity $v(\epsilon)$ of a particle for $d\geqslant 2$ systems. Our approach [4] was to derive a unique transition time T valid for all directions, as well as the corresponding (modified) transition probabilities that agree with the net transition rates predicted for each of the d 1D problems. We found that the period between each jump must be given by [4]

$$T=\tau_B[d-1+\epsilon\coth\epsilon]^{-1}, \tag{14}$$

while the transition probabilities along the field axis and in each of the transverse directions are given by [4]

$$P_\pm=\{(1+e^{\mp 2\epsilon})[\epsilon+(d-1)\tanh\epsilon]/\epsilon\}^{-1}, \tag{15}$$

$$P_\perp=[2(d-1+\epsilon\coth\epsilon)]^{-1}. \tag{16}$$

We showed [4] that these probabilities ($P_\pm$ and $P_\perp$) and time duration (T) give the proper orthogonal diffusion coefficients. However, this approach cannot produce the right free-solution diffusion coefficient along $\hat{\epsilon}$, since it only uses spatial fluctuations. We thus have to generalize the approach presented in the previous section.

Again, we will add a probability to stay put (S') for a period of time (T') in order to introduce implicit fluctuations in the net transition time in the field direction. The elements of this LMC algorithm are thus

$$P'_\pm=\alpha P_\pm,\quad P'_\perp=\alpha P_\perp,\quad T'=\alpha T, \tag{17}$$

with $\alpha=(1-S')$. As far as motion along the field axis $\hat{\epsilon}$ is concerned, this is essentially a 1D problem. Indeed, lateral jumps (described by the probabilities $P'_\perp$ for each of the $d-1$ nonbiased directions) are equivalent to staying put along $\hat{\epsilon}$. Therefore, the total probability of nonmotion along $\hat{\epsilon}$ in d dimensions must be equal to the probability s' to stay put in one dimension,

$$s'=S'+2(d-1)P'_\perp=S'+2(d-1)(1-S')P_\perp. \tag{18}$$

Solving this relation for S' gives

$$S'=(d-1)\epsilon^{-2}-(d-2)\epsilon^{-1}\coth\epsilon-\operatorname{csch}^2\epsilon. \tag{19}$$

The free-solution diffusion coefficient parallel ($\parallel$) to the direction of the field ($\hat{\epsilon}$) is then obtained as described previously in Eq. (13) [using Eqs. (17) and (19)],

$$D_{0_\parallel} = \frac{a^2}{2T'}[P'_+ + P'_- - (P'_+ - P'_-)^2] = \frac{a^2}{2\tau_B}. \qquad (20)$$

This relation will be valid as long as the field is along one of the Cartesian axes. We also stress the fact that the probability to stay put neither affects the calculation of the velocity nor the diffusion coefficient along the orthogonal axes. Although this appears to be the perfect solution to the diffusion problem, there is a major limiting problem: the probability S' is negative for $d \geqslant 3$. In fact, since the solution for S' is unique when we impose a first-passage time interpretation to the dynamics along the field axis (necessary to reproduce Kramers statistics), we must conclude that *it is impossible to design a fixed time-step LMC algorithm that would reproduce both* v_0 *and* D_0 *in more than two dimensions*.

This limitation can be understood when we start from the 1D problem and the relation $2(d-1)P'_\perp + S' = s'$. When we go from 1D to 2D, we reduce the probability to stay put to generate lateral motion. When we go to higher dimensions, we reduce S' further. Obviously, this approach has to be limited to a maximum number of dimensions. Unfortunately, this limit is $d=2$ for all MC square lattice algorithms with jumps made along a single axis per time step, which is very restrictive indeed.

Incidentally, most LMC algorithms commonly used for computer simulations involve low-field approximations of Eqs. (14)–(16). For example, a familiar approach [7] is to use $P_\pm \propto 1 \pm \epsilon$ and a constant time step, which is precisely the first-order approximation of the results derived above. Other algorithms, such as the repton model [5], use a field-dependent time step but are valid only up to $O(\epsilon^2)$.

Discussion. In summary, we demonstrated that temporal fluctuations must be included in lattice random-walk models if the latter are to represent continuous biased diffusion processes. These fluctuations can be introduced in LMC simulations if we replace the constant time step by a stochastic one. We showed how to do this in 1D systems, which is sufficient to perform simulations in any dimension if the clock then advances only when the moves are along the field axis. Our approach allows for the study of the diffusion coefficient for arbitrary fields (note that arbitrary field also means arbitrary coarsening of the lattice mesh size, since ϵ is the relevant field). However, it may be advantageous to have a constant time increment, for example, to use exact methods [3,4] instead of stochastic simulations. We showed how to obtain the value of the probability to stay put (s') that gives the right time variance for 1D systems, and we demonstrated that this solution is unique. Unfortunately, this approach cannot be generalized to more than 2D because S' is then negative. This means that we have to revise the fundamental assumptions of lattice random-walk algorithms.

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