Random walk on a lattice in the presence of obstacles: The short-time transient regime, anomalous diffusion and crowding.

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The diffusion of a particle in a crowded environment typically proceeds through three regimes: for very short times the particle diffuses freely until it collides with an obstacle for the first time, while for very long times diffusion the motion is Fickian with a diffusion coefficient $D$ that depends on the concentration and type of obstacles present in the system. For intermediate times, the mean-square displacement of the particle often increases approximately as $t^\alpha$, with $\alpha < 1$, typical of what is generally called anomalous diffusion. However, it is not clear how one can identify or choose a time or displacement interval that would give a reliable estimate of $\alpha$. In this paper, we use two exact numerical approaches to obtain diffusion data for a simple Lattice Monte Carlo model in both time limits. This allows us to propose an objective definition of the transient regime and a unique value for $\alpha$. Furthermore, our methodology directly gives us the length scale over which the transient regime switches to the steady-state regime. We test our proposed approach using several types of obstacle systems, and we introduce the novel concept of excess diffusion lengths. Finally, we show that the values of the parameters describing the anomalous transient regime depend on the Monte Carlo moves used to describe the dynamics of the particle, and we propose a new algorithm that correctly models the short time diffusion of a particle on a lattice.

I. INTRODUCTION

Diffusive transport taking place in media crowded by immobile and passive obstacles continues to be a source of intense discussions. Diffusion of a particle in such systems should show three regimes. In the first regime the particle simply undergoes free diffusion until it starts colliding with obstacles (this regime is essentially absent in very crowded systems). For long times and large distances, on the other hand, one would expect normal diffusion where the mean square displacement (MSD) increases linearly with time: $\langle r^2(t) \rangle = 2Dt$, with $D$ the diffusion coefficient and $d$ the dimensionality of space. Many researchers characterize the intermediate or transient regime by fitting the data using the expression that defines the concept of anomalous diffusion

$$\langle r^2(t) \rangle = 2dD_\alpha t^\alpha,$$

where $\alpha$ is the anomalous exponent and $D_\alpha$ is often called the anomalous diffusion coefficient although it does not have the proper units unless $\alpha = 1$. We have Fickian diffusion when $\alpha = 1$, anomalous subdiffusion when $\alpha < 1$, and superdiffusion when $\alpha > 1$.

In practice, using eq. 1 to characterize the transient regime of simulation or laboratory data is not trivial. Indeed, it is generally unclear whether there is a range of times for which a unique value of $\alpha$ exists; the presence of error bars can hide the fact that $\alpha$ may be time-dependent (which would make it a much less useful parameter). Identifying the time interval, or equivalently the displacement interval, that one should use to estimate $\alpha$ is often somewhat subjective and non-reproducible. A good example is provided by the work of Ellery et al. in which the anomalous exponent has been estimated by considering a given interval of the transient regime, and then fitting the MSD in that interval in order to get the exponent $\alpha$. In fact that interval was the same for all obstacle concentrations in the medium.

In principle, the transition to the $\alpha = 1$ steady-state occurs when the particle has diffused over distances comparable to the correlation length of the obstacles, $\lambda$, assuming that the system size $L_o > \lambda$. Identifying the limits of the transient regime should thus provide us with an estimate of $\lambda$. The central question is thus how one can objectively define the limits of the transient regime and find a reliable estimate of $\alpha$ and $D_\alpha$.

In this article, we present a detailed analysis of the transition to the steady-state for diffusion on crowded two-dimensional lattices, both for periodically and randomly distributed immobile obstacles. As such lattice models are used to study diffusion in real environments, we also examine the type of Monte Carlo moves that better represent diffusion in the continuum limit. We use two numerical methods that provide us with exact data for short and long times, thus avoiding the pitfalls of fitting data with error bars. We propose an objective way to estimate the value of $\alpha$ and the time at which the transition to normal diffusion takes place. We also propose a way to understand the values of $D_\alpha$ in spite of

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the fact that the units of $D_\alpha$ depend on $\alpha$. Finally, we introduce a new length scale, the excess diffusion length $\beta$, and we show how it is related to the parameters of the transient and steady-state regimes.

This article is structured as follows. In Section II we describe the Lattice Monte Carlo (LMC) model that we use and the various algorithms employed to obtain exact numerical results. In Section III we present the methodology and Data analysis that allows us to obtain our results. Section IV present the different results obtained taking into account the obstacles distributions that we used. We end this paper with a discussion in Section V.

II. METHODS: LMC ALGORITHMS

A. The Random Walk model

We study the diffusion of a particle in the presence of immobile obstacles by using a Monte Carlo model for the random walk of a particle on a two dimensional square lattice with fixed obstacles (see Fig. 1 for two examples). We do not study the role of the particle size, and thus the latter is simply the lattice mesh size.

In the spirit of Lattice Monte Carlo (LMC) models, at each time step the particle can move to a neighbouring site along the $\hat{x}$ or the $\hat{y}$ axis, or stay put. If the selected move makes the particle overlap with an obstacle, the move is rejected but the jump time is added to the clock.

We will be using two versions of this LMC model. In the first one, the probability of staying put is zero and the probability of jumping to each of the four neighbouring sites is thus $\frac{1}{4}$. In the second version, the probability of staying put will be chosen in such a way that we can better represent the short time dynamics of the particle. Both versions are described in Section II B below.

The long-time diffusion coefficient of the particle in a system with periodic boundary conditions (PBC) is calculated using the numerical method described in Section III C. For short times, the MSD is obtained using the Markov chain method described in Section III D.

B. Derivation of the LMC parameters for a free particle (no obstacles)

The theoretical arguments presented here are based on previous work by our group [3]. However, we will not allow diagonal moves because it is unclear how one would then treat collisions with the obstacles. We thus consider a 2D square lattice (Fig. 1) and the jumping probabilities shown in Fig. 2. Since the system is isotropic, we can set $p_{\pm x} = p_{\pm y} = p_1 = \frac{1}{4} (1 - p_o)$, where $p_o$ is the probability of staying put during a LMC iteration. The master equation for the probability $n_{j,l}(t)$ for the particle to be on site $(j,l)$ at time $t$ is

$$n_{j,l}(t + \tau) = p_0 n_{j,l}(t) + p_1 \left[ n_{j-1,l}(t) + n_{j+1,l}(t) + n_{j,l+1}(t) + n_{j,l-1}(t) \right],$$

where $\tau$ is the LMC time step.

The general solution of this system of equations is

$$n_{j,l}(t) = \int_{-\pi/a}^{\pi/a} \int_{-\pi/a}^{\pi/a} C(k_x, k_y) dk_x dk_y \times \exp \left[ ik_x a j + ik_y a l - \omega_d (k_x, k_y) t \right],$$

where $C(k_x, k_y)$ is an arbitrary complex function, $k_x$ and $k_y$ represent the wave number in each of the two directions respectively, and $\omega_d$ is the frequency (the subscript $d$ means that we are in a discrete medium). Substituting eq. (3) into eq. (2) we obtain the dispersion

FIG. 1. The lattice random-walk model studied here. The lattice is of size $25 \times 25$ in this example while the obstacles are of size $2 \times 2$ (in black) and the diffusing particle (in red) is of unit size. Periodic boundary conditions are used. (a) Periodically distributed obstacles with a surface concentration of $\phi = \frac{1}{25}$. (b) Randomly distributed non-overlapping obstacles with the same concentration.

FIG. 2. A schematic of the general 2d LMC algorithm considered in this paper. Only moves to and from site $(j,l)$ are shown. In addition to the traditional axial moves (arrows of medium thickness), there is a probability to stay put (the thickest arrow). $a$ is the length of a site.
relation

\[ \omega_d(k_x, k_y) = -\frac{\ln[p_0 + 2p_1(\cos(k_xa) + \cos(k_ya))] + \frac{\ln 2}{\tau}}{\tau}. \]  

(4)

Considering the solution of the diffusion equation for the longest length scales i.e. for small \( k \), we expand eq. (4) to the fourth order, and using the fact that \( p_0 = 1 - 4p_1 \), we obtain

\[ \omega_d(k_x, k_y) = \frac{p_1 a^2}{\tau} [(k_x^2 + k_y^2) + p_1 a^2 k_x^2 k_y^2 + a^2 \left( \frac{1}{4} p_1 - \frac{1}{2} \right) \times \left( k_x^4 + k_y^4 \right) + O(k^6)] . \]  

(5)

Such lattice models are designed to reproduce the properties of the diffusion equation

\[ \frac{\partial n(x, y, t)}{\partial t} = D_o \left( \frac{\partial^2 n(x, y, t)}{\partial x^2} + \frac{\partial^2 n(x, y, t)}{\partial y^2} \right) , \]  

(6)

where \( D_o \) is the diffusion coefficient for a free particle. The general solution of this equation is

\[ n_{x,y}(t) = \int_{-\infty}^{\infty} \int_{-\infty}^{\infty} C(k_x, k_y) dk_x dk_y \times \exp[i k_x x + i k_y y - \omega_c(k_x, k_y)t] , \]  

(7)

where the subscript \( c \) stands for continuum. From eqs. (6) and (7) we obtain the dispersion relation

\[ \omega_c = D_o (k_x^2 + k_y^2) . \]  

(8)

1. The solution of the diffusion equation and its moments

In two dimensions the solution of the diffusion equation for the initial condition \( n(r, 0) = \delta(r) \) is the Gaussian distribution

\[ n(r, t) = \frac{1}{4\pi D_o t} \exp \left( -\frac{r^2}{4D_o t} \right) , \]  

(9)

The second and fourth moments of this distribution are

\[ \langle r^2(t) \rangle_G = 4D_o t , \]  

\[ \langle r^4(t) \rangle_G = 2 \langle r^2(t) \rangle_G^2 = 32D_o^2 t^2 , \]  

(10)

(11)

where the \( G \) subscript refers to the Gaussian distribution. These two results will now be used to design and test the accuracy of LMC algorithms.

2. The standard LMC algorithm

The simplest LMC algorithm is found when we only match the second order terms in eqs. (5) and (8); this leads to the condition

\[ p_1 a^2 / \tau = D_o . \]  

(12)

Given eq. (10), this relation immediately gives

\[ p_1 = \frac{1}{4} , \]  

(13)

and hence a probability \( p_0 = 0 \) of staying put. In other words, the particle must attempt a move at each time step, and the duration of the latter is

\[ \tau = a^2 / 4D_o . \]  

(14)

This is the standard LMC model described in almost all textbooks and frequently used in research.

In order to better understand the performance of this algorithm, we first evaluate the mean-square displacement of a free particle after \( N \) time steps, \( \langle r^2(N) \rangle = \langle x^2(N) \rangle + \langle y^2(N) \rangle \). In the \( x \)-direction we have

\[ \langle x^2(N) \rangle = \left( \frac{1}{4} (x(N - 1) + a)^2 + \frac{1}{2} (x(N - 1) - a)^2 \right. \]  

\[ + \frac{1}{4} x^2 (N - 1) \]  

\[ = \langle x^2(N - 1) \rangle + \frac{1}{2} a^2 . \]  

(15)

Applying this relation recursively we obtain

\[ \langle x^2(N) \rangle = \frac{1}{2} N a^2 . \]  

(16)

Since \( \langle y^2(N) \rangle = \langle x^2(N) \rangle \), the second moment is simply

\[ \langle r^2(N) \rangle = N a^2 . \]  

(17)

The time duration of \( N \) steps being \( t = N \tau \), eqs. (14) and (17) give \( \langle r^2(N) \rangle = 4D_o t \), which is eq. (10). The standard algorithm thus gives the correct second moment of the distribution of displacements, as expected.

Let us now compute the fourth moment

\[ \langle r^4(N) \rangle = \left( \langle x^2(N) \rangle + \langle y^2(N) \rangle \right)^2 \]  

\[ = \langle x^4(N) \rangle + \langle y^4(N) \rangle + 2 \langle x^2(N) \rangle \langle y^2(N) \rangle . \]  

(18)

We start by calculating

\[ \langle x^4(N) \rangle = \left( \frac{1}{4} x^4(N - 1) + \frac{1}{2} (x(N - 1) + a)^4 \right. \]  

\[ + \frac{1}{4} (x(N - 1) - a)^4 \]  

\[ = \frac{1}{4} a^4 + \langle x^4(N - 1) \rangle \]  

\[ + 3a^2 \langle x^2(N - 1) \rangle . \]  

(19)

Applying this expression recursively, we obtain

\[ \langle x^4(N) \rangle = \frac{1}{4} N (3N - 1) a^4 , \]  

(20)

and similarly for \( \langle y^4(N) \rangle \). The term \( \langle x^2(N) \rangle \langle y^2(N) \rangle \) is more subtle. Here, \( N \) means that a total of \( N \) steps were made with, on average, half of them in each of the
Comparing this result to eq. (11) we obtain

\[
\langle x^2(N) y^2(N) \rangle = \langle x^2(n) y^2(N - n) \rangle_{\text{ens}}
\]

Substituting \(N\) with the nearest obstacle) are key. We will now derive
produce the right second moment, and hence the right
diffusion coefficient at long times, it is not reliable for
This impacts short time dynamics since the first colli-
ions with obstacles are delayed. The standard LMC
This algorithm is frequently used to investigate anomalous
diffusion (see, e.g., Ellery et al [2, 4, 5]); while it does
produce the right second moment, and hence the right
diffusion coefficient at long times, it is not reliable for
short times where first-passage issues (such as colliding
with the nearest obstacle) are key. We will now derive
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4th moment by a term \(\sim 1/t\); as a consequence, the distri-
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3. An improved LMC algorithm

In order to improve upon the standard LMC algo-
rithm, we can try to match both the \(k^2\) and \(k^4\) terms in
eqs. (8) and (5). Since eq. (5) does not include terms
of order \(k^4\), we need to find how to cancel these terms
in eq. (8). However, the cross-product \(p_1^4 k_1^2 k_2^2\) cannot
be eliminated unless \(p_1 = 0\), the trivial solution where
the particle does not move. We thus restrict ourselves
to the other two terms, leading to eq. (12) and

\[
\frac{1}{2} p_1 - \frac{1}{12} = 0 \Rightarrow p_1 = \frac{1}{6} \quad p_0 = \frac{1}{3}.
\]

According to eq. (12) the required time step is then

\[
\tau = a^2 / 6 D_o.
\]

The LMC time step is shorter than for the standard
LMC algorithm, eq. (14), because the particle stays put
with a probability \(p_o = \frac{1}{3}\). The particle thus requires

\[
m = 1 / (1 - p_o) = \frac{3}{2}
\]
time steps, on average, before attempting a jump. Ac-
cordingly, the duration of the LMC steps in this modi-
fied algorithm must be shortened by a factor of \(1/m = 2/3\) in order to keep \(D_o\) constant.

We now compute the second moment:

\[
\langle x^2(N) \rangle = \left\langle \frac{4}{9} x^2(N - 1) + \frac{1}{9} (x(N - 1) + a)^2 + \frac{1}{6} (x(N - 1) - a)^2 \right\rangle = \langle x^2(N - 1) \rangle + \frac{1}{3} a^2.
\]

Applying this expression recursively we obtain

\[
\langle x^2(N) \rangle = \frac{4}{9} N a^2,
\]

and similarly for \(\langle y^2(N) \rangle\). We thus have

\[
\langle x^2(N) \rangle = \frac{4}{9} N a^2.
\]

Since \(N = t / \tau = 6 D t / a^2\), we recover \(\langle r^2(t) \rangle = 4 D t\).

The fourth order moment in \(x\) is given by

\[
\langle x^4(N) \rangle = \left\langle \frac{4}{9} x^4(N - 1) + \frac{1}{9} (x(N - 1) + a)^4 + \frac{1}{6} (x(N - 1) - a)^4 \right\rangle = \langle x^4(N - 1) \rangle + 2 a^2 \langle x^2(N - 1) \rangle + \frac{1}{3} a^4.
\]

Applying this expression recursively we obtain

\[
\langle x^4(N) \rangle = \frac{1}{9} N^2 a^4.
\]
and similarly for $\langle y^4(N) \rangle$. Once again, the only remaining part to be calculated in eq. (18) is the cross-correlation $\langle x^2(N)y^2(N) \rangle$. Here, if the particle makes $n$ steps in the $x$ direction, it must make $N-n-n_o$ steps in the $y$ direction, where $n_o$ is the number of times the particle stayed put. We can thus write

$$\langle x^2(N)y^2(N) \rangle = \langle \langle \langle x^2(n)y^2(N-n-n_o) \rangle_{ens} \rangle_{w} \rangle_{n,n_o}$$

$$= \langle n_0^2(N-n-n_o)a^2 \rangle_{n,n_o}$$

$$= \left( N \langle n \rangle_n - \langle n_0 \rangle_{n,n_o} \right) - \langle n^2 \rangle_n a^4.$$

(36)

We can use eq. (23) to compute two of the terms, but the probability $q_N(n)$ is now given by:

$$q_N(n) = \frac{N!}{n!N-n!} \left( \frac{1}{3} \right)^n \left( \frac{2}{3} \right)^{N-n}.$$

(37)

This gives

$$\langle n \rangle_n = \frac{1}{2} N; \quad \langle n^2 \rangle_n = \frac{1}{3} N(N+2).$$

(38)

Calculating $\langle n_0 \rangle_{n,n_o}$ requires the joint probability $q_N(n,n_0)$ of having a walk with $n$ jumps in the $\hat{x}$ direction and $n_0$ iterations without a jump:

$$\langle n_0 \rangle_{n,n_o} = \sum_{n=0}^{N} \sum_{n_0=0}^{N-n} q_N(n,n_0)n_0.$$  

(39)

Since the particle has three equally probable choices at each step (i.e., moving in the $\hat{x}$-direction, the $\hat{y}$-direction or not moving), the probability $q_N(n,n_0)$ is simply

$$q_N(n,n_0) = \frac{N!}{n!n_0!(N-n-n_0)!} \left( \frac{1}{3} \right)^N.$$  

(40)

Using this function, we obtain

$$\langle n,n_0 \rangle_{n,n_o} = \frac{1}{3} N(N-1).$$  

(41)

The cross-correlation term is thus given by

$$\langle x^2(N)y^2(N) \rangle = \frac{1}{6} N^2 a^4 - \frac{1}{6} N(N-1)a^4 - \frac{1}{3} N(N+2)a^4$$

$$= \frac{1}{6} N(N-1)a^4.$$  

(42)

Substituting eqs. (45) and (42) in (18), we get

$$\langle r^4(N) \rangle = \frac{2}{5} (4N^2 - N) a^4.$$  

(43)

Since $N = t/\tau$ and $\tau = a^2/(6D_o)$, we can write

$$\langle r^4(t) \rangle = 32 D_o^2 a^2 \tau^2 - \frac{3}{2} a^2 D_o \tau.$$  

(44)

Comparing with eq. (11) we obtain

$$\frac{\langle r^4(t) \rangle}{\langle r^4(t) \rangle_G} = 1 - \frac{a^2}{24 D_o \tau}.$$  

(45)

Just like in eq. (27), we have the correct leading term for the fourth moment, but the $\sim 1/\tau$ correction term is now three times smaller. This alternative algorithm, which allows the particle to stay put during a LMC step, is thus better at capturing short time dynamics. Although it is possible to eliminate the $\sim 1/\tau$ correction term by allowing diagonal jumps [3], this would lead to unclear difficulties when treating collisions with obstacles.

C. Long time Exact solution for LMC algorithms

To compute the long time particle diffusivity, we use the numerical method introduced in [6, 7] since it produces exact results when using PBCs. The idea is that while the diffusion coefficient $D_o$ along $\hat{x}$ is not readily accessible for most obstacle configurations, it is relatively easy to calculate the particle’s reduced velocity $v_x/v_{zo}$ in the presence of an external force oriented along $\hat{x}$ ($v_{zo}$ is the velocity in absence of obstacles). The diffusivity is then obtained via the Nernst-Einstein relation $D_x/D_{zo} = v_x/v_{zo}$ in the zero-force limit.

Velocity calculations can be reduced to solving a set of $N$ coupled linear equations, where $N$ is the number of available lattice sites. These equations can be written as a transition matrix $T$ containing the jumping probabilities between the different lattice sites. We have previously shown that it is possible to algebraically simplify the matrix problem and the passage to the zero-force limit such that the only remaining step is the numerical inversion of a matrix. Note that in the presence of disorder, the final diffusivity must also be averaged over an ensemble of different obstacle configurations. The numerical procedures are fully described in [6, 7].

D. Markov process

A Markov process is characterized by the fact that predicting the next state of the system only requires information about the present state, i.e., there are no memory effect. Symbolically, it is thus possible to write

$$|p(t+1)\rangle = |p(t)\rangle = ... = T^t |p(t=0)\rangle,$$  

(46)

where $|p(t)\rangle$ is the state of the system at step $t \in \mathbb{N}$ and $T$ is the transition matrix defining the evolution of $|p\rangle$. For our diffusion problem, $|p(t)\rangle$ is a vector that includes the probability for the particle to be on each of the accessible lattice sites at time $t$, $|p(0)\rangle$ is the initial location of the particle, and $T$ is a matrix that contains the jumping probabilities for the chosen LMC process. The $1 \times 1$ particle has access to $L_o^2 (1 - \phi)$ sites, where $L_o$ is the size of the lattice. In practice, we use a large value $L_o = 500$. Since we start the particle in the centre,
the value of $t$ is limited to about 249 since we cannot use PBC here. For systems with large correlation lengths $\lambda$, larger lattices may be needed to study the initial stages of diffusion via this approach. From the state vector $|p(t)\rangle$, one can easily obtain the exact distribution of displacement at time $t$ and all of its moments.

III. METHODS: DATA ANALYSIS

We now introduce our methodology and test it using a system of $2 \times 2$ obstacles placed periodically in $5 \times 5$ primitive cells, giving $\phi = \frac{4}{25}$ (Fig. 1b). From now on, numerical data will be given using the mesh size $a$ as the unit of length, times will be in units of $a^2/D_\alpha$ and diffusion coefficients will be in units of $D_\alpha$.

A. Plotting MSD data

Although the particle can start from 21 different initial positions in the primitive cell, only 5 of these are unique. Figure 3 shows two different log-log representations of the time evolution of the MSD, both for each of these 5 sites individually and for the MSD averaged over all 21 initial sites. The $\langle r^2(t) \rangle$ vs. $t$ plot, Fig. 3a, is clearly not useful. Instead, it is better to plot the diffusion ratio $\langle r^2(t) \rangle / 4t$ vs. $t$, Fig. 3b, as we then see clear features. Since $\lim_{t \to \infty} \langle r^2(t) \rangle / 4t = D$, this plot also provides us with an estimate of the long-time diffusion coefficient.

Let us examine Fig. 3 in detail. The MSD curves start from two different values after the first step (solid lines); this is because some starting sites are adjacent to an obstacle, while most are not. In the latter case, we find $D = 1$ because the particle behaves initially as a free particle until it hits an obstacle. The other value is lower since the particle then starts next to an obstacle and can thus hit it immediately. Such MSD curves correspond to experimental situations where all the particles of a sample start from the same location. When we average over all possible starting positions, which is equivalent to having a sample in equilibrium with the medium (the most common assumption), we obtain the dashed curve. All curves converge to the value of the exact long-time diffusion coefficient, as expected. However, it is clear that the intermediate regime greatly depends on the initial state of the system: none of the solid curves behave like the dashed curve, and two of them are even non-monotonic. It is simply not possible to define an anomalous exponent $\alpha$ for the solid curves.

As mentioned above, a uniform initial distribution (the dashed curve) is the standard choice. We will thus analyze this data to identify the intermediate and steady-state regimes. In order to estimate the anomalous exponent $\alpha$, we rewrite eq. (1) as:

$$\log \left( \frac{\langle r^2(t) \rangle}{4t} \right) = (\alpha - 1) \log(t) + \log(D_\alpha).$$

(47)

If there is indeed a regime where eq. (1) applies, then it should show up as a straight line with a (negative) slope of $\alpha - 1$; however, it is not obvious where it is located in Fig. 3, or even if it exists at all.

B. Estimating the anomalous exponent $\alpha$

Figure 4 shows the same data together with the construct that we propose to estimate $\alpha$ and locate the transition to the steady-state. The only non-arbitrary point that can be identified here is the inflection point separating short times (positive second derivative) and long times (negative second derivative). In our opinion, this should define the centre of the intermediate regime. Accordingly, the tangent at the inflection point can be used to estimate the values of $\alpha$ and $D_\alpha$.

The intersection between this tangent and the long-time plateau can be used to define the crossover time $t^*$ at which the intermediate regime transitions into the

![Graph](image-url)
steady-state (the corresponding length scale is \( r^* = \sqrt{4D\tau^*} \)). This approach is not arbitrary and allows us to uniquely characterize the transient phase in absence of a clear linear regime in Fig. 3. 

It is easy to find the location of the crossover in terms of the parameters describing the transient and steady-state regimes. Indeed, by construction, the crossover time \( t^* \) is the solution of eq. (47) where we replace the \( lhs \) by \( \log(D) \). The solution is simply

\[
t^* = \left( \frac{D_\alpha}{D} \right)^{1-\alpha},
\]

which directly leads to

\[
r^* = 4 \left( \frac{D_\alpha}{D} \right)^{1-\alpha}.
\]

Another interpretation of the crossover time will be in Section III D.

\[
FIG. 4. Diffusion ratio \( \langle r^2(t) \rangle /t \) as a function of time. We also show the inflection point, the tangent used to estimate the anomalous exponent \( \alpha = 0.95662 \) and the value of the fitting parameter \( D_\alpha = 0.85172 \), the long-time diffusion plateau \( D = 0.79143 \), and the crossover point.
\]

C. Excess short-time diffusion

Diffusion is normal at long times: we then have \( \alpha = 1 \) in eq. (1). However, a particle initially diffuses faster because it takes several collisions with the obstacles to go from \( D_\alpha = 1 \) to a steady state value \( D < 1 \). Indeed, all the data points are above the plateau value in Fig. 4. Therefore, in order to properly fit long time data and obtain a good value for \( D \), we must use the expression

\[
\langle r^2(t) \rangle = 4Dt + \beta^2,
\]

where \( \beta \) is the excess diffusion length due to the transient regime. Figure 5 presents a plot of \( \beta \) vs. \( 1/\sqrt{t} \) for our example. The plateau value \( \beta = 0.55215 \) is reached at \( t \approx t^* \). The length scale \( \beta \) measures the importance of the transient, anomalous diffusion regime: \( \beta < 1 \) means that this regime has minimal importance, while values larger than the mean distance between obstacles would indicate long length scale effects.

One can also rewrite eq. (50) as

\[
\langle r^2(t) \rangle = 4D(t + \tau_\beta),
\]

where

\[
\tau_\beta = \beta^2 /AD
\]

is the apparent excess time due to anomalous diffusion.

\[
FIG. 5. Time evolution of the excess diffusion length \( \beta \). The vertical dash line indicates the crossover time \( t^* \). The asymptotic value is \( \beta = 0.55215 \), which corresponds to an excess time of \( \tau_\beta = 0.17442 \).
\]

D. Giving a physical meaning to \( D_\alpha \)

Clearly \( D_\alpha \) is not a diffusion coefficient since its units depend on \( \alpha \). Therefore, we cannot plot \( D_\alpha \) vs. system parameters like \( \phi \) (each data point would have its own unit of measurement). However, we may get useful information from the fitting parameters if we use a fitting function with proper units to replace eq. (1), such as

\[
\langle r^2(t) \rangle = 4Dt \left( \frac{t}{t_\alpha} \right)^{\alpha - 1},
\]

where the new fitting parameter \( t_\alpha \) (replacing \( D_\alpha \)) is the time needed to anomalously diffuse over a distance \( r_\alpha = \sqrt{4Dt_\alpha} \), i.e., the displacement that would have been achieved via normal diffusion (in other words, \( r_\alpha^2 = 4Dt_\alpha = 4D_\alpha t_\alpha^\alpha \)). But this is in fact the very definition of the crossover time in Fig. 4. Indeed, it is
easy to prove mathematically that $t_\alpha = t^*$ and $r_\alpha = r^*$. Alternatively, it is also possible to replace eq. (1) by

$$\langle r^2(t) \rangle = r_\alpha^2 \left( \frac{4Dt}{r_\alpha^2} \right)^\alpha,$$

(54)

where $r_\alpha = r^*$ would then replace $D_\alpha$ as the fitting parameter. However, eq. (53) is more intuitive.

In conclusion, the two physically meaningful fitting parameters are the anomalous exponent $\alpha$ and either the crossover time $t^*$ or the crossover distance $r^*$ (but not the oddly dimensioned parameter $D_\alpha$). We will be looking at both options in the Results section.

E. Comparing the two Monte Carlo Algorithms

Figure 6 presents the MSD data obtained from both LMC algorithms; as expected they differ only at short times. Because the value of the correction factor for $\langle r^2(t) \rangle$ is three times higher with the standard LMC algorithm, the first collisions are delayed and the diffusion ratio $\langle r^2 \rangle / 4t$ is larger even slightly beyond the inflection point. The value of $\alpha$ is thus smaller with the standard LMC algorithm and the crossover distances $r^*$ and times $t^*$ are slightly underestimated.

It is interesting to note that this effect is sometimes inverted at high concentration when we have randomly distributed obstacles (see Chapter 3). In such cases, we believe that the fact that larger displacements are slightly less probable with the standard algorithm leads to longer trapping times in dense areas and hence smaller diffusion ratios $\langle r^2 \rangle / 4t$ (this is currently under investigation).

IV. RESULTS

The data presented in this section were obtained using a square lattice of size 500 x 500 (for both short and long time calculations). We investigate various obstacle concentrations for three different obstacle sizes, namely $1 \times 1, 2 \times 2$ and $3 \times 3$. We also compare periodic and random distributions of obstacles. For periodic systems of obstacles, the data is averaged over all possible starting positions in the periodic cell. For random systems, we average over 600 different realizations of the system of obstacles, and the starting position of the particle for the Markov chain is chosen randomly in a $10 \times 10$ box located in the centre of the lattice. We generally keep the obstacle concentration in the range $\phi \in [0.0, 0.4]$ to avoid problems with percolation thresholds [7].

A. The asymptotic diffusion coefficient $D$

Figures 7 shows how the diffusivity $D$ varies with $\phi$. These results are in agreement with previous studies (see, e.g., [7,8]). For a given concentration $\phi$, large obstacles have less impact than small ones because aggregating obstacles increases the percolation threshold and leaves wider passages for the particle to migrate through. Our results also agree with the known value of the percolation threshold $\phi^* \approx 0.7254\%$ for unit size obstacles [7]. Note that the curvature of the $D(\phi)$ plots changes from positive for periodic obstacles to negative for random ones, a qualitative difference that we will see again later. As we showed in [8], we can get zero curvature (so that $D$ is a linear function of $\phi$) by creating fuzzy obstacle distributions.

B. The excess diffusion length $\beta$

As mentioned before, the length scale $\beta$ can be used to measure the importance of the transient regime. Looking at Fig. 4, we can see that the area between the data points and the $D$ plateau, which is related to $\beta$, can increase either because $D$ decreases or because the crossover time $t^*$ decreases.

The random system is simpler, Fig. 8: $\beta$ increases with concentration because $D$ decreases as $\phi$ increases, while both $t^*$ and $r^*$ increase because the correlation length of the obstacle distribution increases with $\phi$ (see section IV D). We note that the curves cross each other; this is due to the fact that the percolation threshold is larger for larger obstacles, which leads to a crossover time that diverges at lower concentrations for smaller obstacles (see Fig. 10). Not surprisingly, we observe a very sharp increase of the excess diffusion time $\tau_\beta = \ldots$
\[ \beta^2/4D \] when we approach the percolation concentration in Fig. 8, since \( \beta \) increases while \( D \) decreases.

Figure 8 shows that systems with periodic obstacles are very different: indeed, \( \beta(\phi) \) is now a non-monotonic function. Here, as the concentration increases, both the diffusivity and the crossover time \( t^* \) decrease. The competition between these two factors give a maximum at a critical value \( \phi^* \) which depends on obstacle size. When \( \phi < \phi^* \), \( t^* \) is large but the exponent \( \alpha \) is close to unity and anomalous diffusion becomes unimportant. When \( \phi > \phi^* \), on the other hand, although \( \alpha \) decreases, the corresponding anomalous diffusion takes place over very short time periods \( t^* \) and the effect also decreases.

The difference between the periodic and random cases is striking and clearly demonstrates that obstacle placement can have a profound qualitative effect on diffusion. The excess diffusion length \( \beta \) and time \( \tau_\beta \) provide useful information about the nature of the diffusion process in these systems as they behave in completely different ways when the obstacle concentration increases.

C. The anomalous exponent \( \alpha \)

The exponent \( \alpha \) is often the main (or even the sole) parameter used to describe the transient or anomalous diffusion regime. Figure 9 shows how \( \alpha \) varies with the obstacle concentration \( \phi \). Similar to the diffusivity \( D(\phi) \) in Fig. 7, the \( \alpha(\phi) \) curves have a positive curvature for periodic systems but a negative one for random systems. We note that \( \alpha \) has a very weak dependence on obstacle size for periodic systems. However, for random systems, the value of \( \alpha \) drops and becomes dependent upon obstacle size at higher concentrations because we then get close to the percolation threshold. The exponent is smaller for random systems, confirming that diffusion is more anomalous in the presence of disorder. Overall, the data shown in Fig. 9 is similar to that of Fig. 3 in [8]; however, our results demonstrate that the
curves do not cross at low concentrations.

![Graph](image)

**FIG. 9.** Anomalous exponent $\alpha$ vs. obstacle concentration $\phi$ for three different obstacle sizes. (a) Periodically, and (b) randomly distributed obstacles.

D. The crossover: time $t^*$ and length $r^*$

As mentioned previously, the transition between the anomalous and normal diffusion regimes can be characterized by a crossover time $t^*$ and a crossover length $r^*$ (these parameters are easily found using the approach described in Fig. 4). Moreover, these two variables can advantageously be used to replace the fitting parameter $D_o$ since they have proper dimensions. In this section, we will examine them with this dual role in mind.

For periodic systems, $r^*$ trivially decreases as $\phi$ increases, Fig. 10(b), since the distance between the obstacles plays the role of the correlation length and is essentially the distance the particle needs to travel before reaching the steady-state. Not surprisingly, the related crossover time, Fig. 11(a), follows the same pattern.

![Graph](image)

**FIG. 10.** Crossover length scales $r^*$ vs. obstacle concentration $\phi$ for three different obstacle sizes. (a) Periodically and (b) randomly distributed obstacles.

E. The relation between the length scales $\beta$ and $r^*$

In diffusion problems of the kind studied here, the physics is controlled by a single length scale, the correlation length (or crossover length). Therefore, there must be a relation between the excess diffusion length $\beta$ and the crossover length $r^*$. As mentioned before, $\beta$, the constant term in the linear fit of the asymptotic (normal diffusion) behavior of the MSD, essentially measures the additional displacement due to the fact that diffusion is faster in the transient regime. We can define the instantaneous rate of diffusion as $\rho(t) = \partial(r^2(t))/\partial t$; we note that $\rho = 4D$ when we have normal diffusion, and
We have reproduced this best fit on Fig. 12, where we show the data for randomly distributed obstacle systems. Again, the data for the three different obstacle sizes collapse to form a single curve, and the dashed line is in excellent agreement with the data to $\beta \approx 2.5$. Beyond that point, $\beta$ grows more slowly than what this simple theory predicts, suggesting that additional factors play a role as we approach percolation.

We thus showed that indeed there is a single characteristic length scale in the problem, and that the function $A(\alpha)$ given by eq. 14 allows us to collapse all the data, for periodic and random systems and for obstacles with different sizes, onto a single universal curve.

The excess diffusion length $\beta$, which is almost always neglected, thus contains useful (and universal) information about a crowded system.

\begin{equation}
\rho = 4 \alpha D_\alpha t^{\alpha - 1}
\end{equation}

The two rates are equal at time

\[ t_c = \alpha^{1/(1-\alpha)} t^* . \]  

For $t < t_c$, anomalous diffusion is faster than normal diffusion but slows down up to time $t_c$. It is during this period of time that the excess diffusion $\beta$ builds up. We can thus estimate $\beta$ as

\begin{equation}
\beta^2 \approx 4 D_\alpha t^*_c - 4 D t_c = A(\alpha) r^* \alpha^2, \tag{56}
\end{equation}

where

\[ A(\alpha) = (1 - \alpha)\alpha^{(1-\alpha)} . \tag{57} \]

Interestingly, this approximate relation between $\beta$ and $r^*$ is a function of the anomalous exponent $\alpha$ and nothing else. We also note that $A(\alpha = 1) = 0$, as expected since diffusion is then normal $\forall t \geq 0$.

In Fig. 12 we plot our data to show $\beta$ vs $r^* \sqrt{A(\alpha)}$, for both random and periodic distributions of obstacles, in order to check the accuracy of this estimate. For periodic obstacle systems, Fig. 12, all data points collapse on a line of slope $1.056$, in excellent agreement with our estimate. This is quite remarkable given the fact that $\beta(\phi)$ is a non-monotonic function of $\phi$, but we estimate $\beta$.

\begin{align*}
\text{Obstacle concentration } \phi & \quad (a) \quad \text{Periodically, and (b) randomly distributed obstacles.} \\
\text{Obstacle concentration } \phi & \quad (b) \quad \text{Excess diffusion length } \beta \text{ vs. } r^* \sqrt{A(\alpha)} \text{ for three different obstacle sizes.} 
\end{align*}

\begin{align*}
\text{Obstacle concentration } \phi & \quad (a) \quad \text{Crossover time scales } t^* \text{ vs. obstacle concentration } \phi \text{ for three different obstacle sizes.} \\
\text{Obstacle concentration } \phi & \quad (b) \quad \text{Crossover time scales } t^* \text{ vs. obstacle concentration } \phi \text{ for three different obstacle sizes.}
\end{align*}

\begin{align*}
\text{Obstacle concentration } \phi & \quad (a) \quad \text{Crossover time scales } t^* \text{ vs. obstacle concentration } \phi \text{ for three different obstacle sizes.} \\
\text{Obstacle concentration } \phi & \quad (b) \quad \text{Crossover time scales } t^* \text{ vs. obstacle concentration } \phi \text{ for three different obstacle sizes.}
\end{align*}

V. DISCUSSION

In this paper, we have revisited the classical problem of the nature and properties of the transient regime for a particle diffusing on a lattice populated by immobile obstacles. We first showed that the standard Monte Carlo...
algorithm suffers from a narrower than expected displacement distribution function for short times. Since the properties of the transient regime depend on the precise timing of the first few collisions with obstacles, we proposed an improved LMC algorithm; however, more work has to be done since our algorithm also suffers from the same problem, albeit to a lesser extent. Introducing the diagonal jumps remains necessary.

Generally speaking, one can expect a transient regime with two sub-regimes. In some low-density cases, diffusing particles may take a non-negligible amount of time to collide with a first obstacle: during that period, one has essentially free diffusion. After the particles have started colliding with obstacles, their instantaneous diffusion coefficient decreases; the steady-state regime is reached when the particle has diffused over a length scale that characterizes the environment, e.g., the mean distance between nearest-neighbour obstacles when the latter are periodically distributed, or the correlation length of a random distribution.

Several authors have characterized the second part of the transient regime using the concept of anomalous diffusion, i.e. by fitting the MSD data using \( \text{eq. 1} \). However, this raises the question of identifying the limits of the regime where this might apply since the value of the anomalous exponent \( \alpha \) depends on the time interval chosen (not to mention the nature of the LMC algorithm). We used two numerical approaches in order to obtain extremely precise data and test our understanding of this often neglected issue. Our short-time MSD data came from a Markov chain methodology, which is equivalent to doing Monte Carlo simulations with an infinite ensemble size, while our exact matrix method provided the steady-state diffusion coefficients.

Our data showed that here is no time interval where eq. \( \text{1} \) applies perfectly, in the sense that a log-log plot of the MSD, \( \langle r^2(t) \rangle \), vs time \( t \) does not show a regime where the data falls on a straight line with a slope \( \alpha \). Nevertheless, the concept of anomalous diffusion remains a useful tool to characterize the transient regime. We thus proposed to define the centre of this regime as the inflection point in the log-log plot of \( \langle r^2(t) \rangle / 4t \), vs \( t \); this has the key advantage of being a well-defined and objective location. The anomalous exponent \( \alpha \) is then simply related to the slope at the inflection point and this leads to straightforward and natural definitions for the crossover time \( t^* \) and crossover length \( r^* \). We also argued that these two parameters should be used to replace the traditional fitting parameter \( D_\alpha \) since the latter has no physical meaning (e.g., the units of measurement of \( D_\alpha \sim cm^2/sec^\alpha \) depend on \( \alpha \)).

Using our improved LMC algorithm, the two numerical methods mentioned above and our definition for the transient regime and its parameters, we examined the physics of periodic and random distributions of obstacles of different sizes. We focused our work on these two factors as previous studies have shown their importance. For example, Ellery et al. [2] recently stressed the fact that the size of the obstacles plays a major role for a given surface coverage \( \phi \). We previously showed that the degree of randomness of the distribution of obstacles also has a major impact for a given \( \phi \).

The asymptotic diffusion coefficient \( D \) and the anomalous exponent \( \alpha \) show similar dependence upon the surface concentration \( \phi \); while \( D(\phi) \) and \( \alpha(\phi) \) are concave functions for periodic arrays of obstacles, they are convex functions for random ones. This shows the importance of the precise distribution of obstacles in such systems (in a previous paper [8], we showed that it is possible to design fuzzy obstacle systems for which the function \( D(\alpha) \) is linear). We also noticed that small obstacles have a much larger impact than large ones for random distributions (but not for periodic ones), in agreement with the recent results by Ellery and co-workers; this difference between periodic and random distributions is due to the presence of a percolation threshold \( \phi^* \) in the latter case, with \( \phi^* \) increasing with obstacle size.

For periodic distributions of obstacles, the crossover distance \( r^* \) trivially decreases when \( \phi \) increases or the obstacles get smaller because the latter then get closer to each other while the geometric features remain unchanged. Not surprisingly, we observe the very same behavior for the crossover time \( t^* \). For random distributions of obstacles, however, both \( r^* \) and \( t^* \) increase with concentration as we get closer to percolation. In this case, it is not the mean distance between obstacles that matter, but the size of the obstacle aggregates (which is measured by the correlation length) that form as \( \phi \) increases.

In order to extract the diffusion coefficient \( D \) from laboratory or via simulation data, it is customary to fit long-time data points on a \( \langle r^2(t) \rangle \) vs. time \( t \) plot using eq. \( \text{50} \). The constant \( \beta \), which is a length scale, is almost always ignored. Our study of \( \beta \) showed that it increases with \( \phi \) for random systems, but that it is a non-monotonic function of \( \phi \) for periodic arrays of obstacles. In the former case, \( \beta \) simply follows the correlation length, while in the latter case the result can be explained by the competition between two competing factors (namely, the reduced impact of obstacles as their separation increases). We suggests that the excess diffusion \( \beta \) is a measure of the importance of anomalous diffusion in a system.

It is well-known, however, that the physics of diffusion in systems of immobile obstacles should be related to a single length scale, e.g. the crossover length \( r^* \). This raises the question of the relation between the length scales \( \beta \) and \( r^* \) for a given system. We have proposed a simple approximate relation between the two, eqs. [56]
and a relation that includes only the anomalous exponent $\alpha$. Remarkably, this relation is excellent for periodic distributions of obstacles (whatever the size of the obstacles is) in spite of the fact that $r^*(\phi)$ is a monotonic function of $\phi$ while $\beta(\phi)$ is not, a very interesting and surprising result. The same relation allows us to collapse the data for all three obstacle sizes on a universal curve when the obstacles are randomly distributed; however, it underestimates the value of $\beta$ when the concentration $\phi^*$ increases above $\approx 15\%$. Our study thus supports the idea that there is a direct relation between the two length scales (obviously, it is also possible to establish a similar connection between the time scales $\tau_\beta$ and $t^*$). Moreover, the function $A(\alpha)$, eq. [56], may be used in some cases to estimate $\alpha$ when both $r^*$ and $\beta$ are obtained through fits, as is often the case.

In conclusion, we have described a new methodology to better analyze the transient regime using the concept of anomalous diffusion, and we have designed an improved LMC algorithm for diffusion on a square lattice. While there is no time regime where $\langle r^2 \rangle \sim t^\alpha$, it is possible to obtain excellent results by using an inflection point as the basis of the analysis. We have also introduced the excess diffusion length scale $\beta$ in order to quantify the importance of the transient regime, and we have shown that there is a direct and universal relation between $\beta$ and the crossover length scale $r^*$. The fact that the ratio $\beta/r^*$ depends only on the anomalous exponent $\alpha$ may be used to conclude that the concept of anomalous diffusion provides a useful way to analyze the transient regime. Our analysis of the transient regime showed that periodic and random distributions of obstacles give qualitatively different results for all parameters used to describe the physics. However, in a real system like a biomembrane the obstacles are neither perfectly random nor perfectly periodic. It will be interesting to examine how these parameters evolve in systems with a tunable amount of disorder (in progress).

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