

Particle Separation Using High Frequency Alternating External Fields

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We present results for a model that describes particle penetration through a medium. The particle motion is subjected to an alternating external field (bias). We employ theoretical considerations and computer simulations. A random walk model is utilized with an alternating bias factor in the probabilities of jumps, which selectively changes the mode of motion from a pure random walk to a regular ballistic, and the entire range in between. At relatively low bias values, a slower diffusion drift accompanies the particle oscillations. Thus, the particle can penetrate deeper into the bulk of the system. On the other hand, if the bias is sufficiently high, the random walk becomes forbidden. Under these conditions, the alternating bias forces particles to undergo a pure ballistic motion, oscillating inside a limited region of space, thus not being able to penetrate deeper into the system. We find that the threshold condition for the transition from random walk to ballistic motion is very sharp. Therefore, it is possible to separate different particles by adjusting bias to overshoot the jump probability of one sort of them and at the same time to be under the jump probability of the other sort of particles. This result could be of importance to explain the high sensibility of penetration through membranes.

Introduction

Particle separation is a very important process from the industrial point of view with a plethora of applications, such as in the separation of grains, in biosensors,¹ in microchips,² and so forth. One direct approach to achieve separation between two different entities would be to find some conditions under which different particles would move with different velocities or, even better, one species would remain trapped in certain regions of space while the others would continue to move.

One of the challenges in contemporary science is the problem of selective penetration of particles through membranes. This permits one to isolate some components of complex blends and mixtures. The usual explanation of how it happens is the assumption that the penetrating substance has a relatively high diffusion coefficient through the membrane, while other substances have almost zero diffusivity there. Membranes of living cells are extremely sensitive and can separate some materials which have quite similar properties and similar diffusion coefficients. To explain this idea, we use results of our previous model^{9–11} on random walks in disordered media,

which includes a bias factor that increases motion in a specific direction. The main point is that the bias (say, some external electric field) changes its direction at a given frequency, ν . One could then expect that under certain conditions the alternating bias will contribute to the separation of particles.

Nonsymmetric diffusion has been used to describe many properties of matter (see for example ref 11 and literature cited there). In many models, the nonsymmetric behavior is due to the retention of memory of the previous step, resulting in enhanced diffusion. In our previous work,^{10,11} this was due to an external field leading to a ballistic motion in the long time limit. On the other hand, when the bias alternates at a given frequency $\nu = 1/2\tau$ (τ is the time it takes to change the direction of the bias) the mean square displacement was found to be proportional to time t , a behavior typical of a stochastic random walk. It was further found that the proportionality coefficient (diffusion coefficient) increases with τ .

It is now interesting to investigate how an alternating field (in time and/or in space) could lead to a regular random walk motion in one limit or to a continuous drift on the other limit. Moreover, we note that diffusion-like motion results from a time alternating bias,¹¹ which is typical of a deterministic system. On the other hand, drift motion appears when a space (and time) alternating potential (so-called ratchet potential) is applied (see refs 12 and 13 and literature cited there). In particular, in ref 13 it was demonstrated that a ratchet potential is capable of converting unbiased random fluctuations into directed motion if, on the average, all acting forces and temperature gradients are zero.

Earlier,^{10,11} we found that if a bias is applied, then there is a crossover time after which the mode of motion switches from a predominantly random walk to a ballistic one. The transition time depends on the jump probability and the height of the bias. It is natural to expect that at large

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values of bias the transition time will be very short. Therefore, high bias alternating at high frequency will catch the particles and cause them to vibrate at a given distance from the origin and never penetrate deeper into the system. If the bias threshold for this effect is very sharp, some other, quite similar particles could be subjected to a random walk, so that under the same external field they will be able to penetrate the system. The main task of the present article is to test how sharp the transition region is and whether an alternating external field could be an effective method for particle separation.

The Model

We describe diffusion in a certain medium using a random walk model on a one-dimensional lattice. As previously,^{9–11} we use a lattice which is generated in such a way so that every two neighboring sites (i, j) are connected with a channel, the motion along which is prescribed by a given probability $p_{i,j}$ ($j = i \pm 1$). In a sense, this means that the particle has to overcome a given energy barrier. The height $E_{i,j}$ of the barriers (or the probabilities $p_{i,j}$) is constant and remains unchanged during the run. There is also a finite probability of no jump, which is given by

$$p_{i,i} = 1 - \sum_{j \neq i} p_{i,j} \quad (1)$$

We now apply some external bias. For instance, this could represent the case of a membrane serving as an electrode, on which an electric field is applied to the internal and external parts of it. In terms of probabilities, this means that the overall probability p^+ to jump along the bias is increased by the bias probability p_b , while the probability p^- to jump opposite the bias is reduced by the same amount.

$$p^{\pm} = \begin{cases} 1 & \text{if } p_{i,i+1} + p_b > 1 \\ p_{i,i+1} + p_b & \text{if } 0 \leq p_{i,i+1} + p_b \leq 1 \\ 0 & \text{if } p_{i,i+1} + p_b < 0 \end{cases} \quad (2)$$

$$p^{\pm} = \begin{cases} 1 & \text{if } p_{i,i-1} - p_b > 1 \\ p_{i,i-1} - p_b & \text{if } 0 \leq p_{i,i-1} - p_b \leq 1 \\ 0 & \text{if } p_{i,i-1} - p_b < 0 \end{cases}$$

After $\tau = 1/2\nu$ steps, the sign of p_b is reversed. The plus sign pertains to the motion along the direction of bias, while the minus sign is for the one opposite to the bias. Precaution is taken to keep the p^+/p^- values within the $[0-1]$ range. The starting point is the site $i = 1$. A jump to the right increases i by 1, and a jump to the left decreases it by 1. There is a boundary condition that jumps to the left of site $i = 1$ do not change i because $i = 1$ is the starting position of the membrane. This is to say that if the particle leaves the membrane, immediately it returns to the starting point and continues its attempt to penetrate. During the computation, the time t and the span h (in lattice units) are monitored. Specifically, we monitor the fraction $f(h) = n(h)/N$, which gives the ratio of how many times $n(h)$ out of N attempts the particle has succeeded in crossing a membrane of thickness h , for various values of $p_{i,j}$, p_b , and τ .

Results

We have found earlier^{9–11} that there is an interplay between pure ballistic motion and a stochastic random walk, which depends on the values of the bias and the

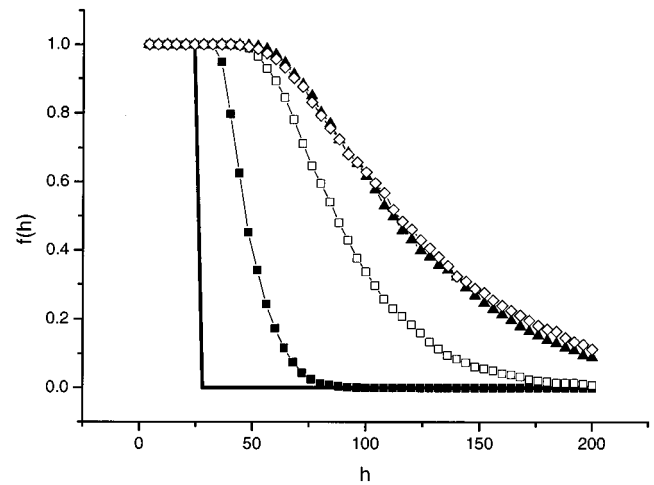


Figure 1. Fraction $f(h)$ of particles that propagate to distance h . The frequency is $1/50$ ($\tau = 25$), $p_{i,j} = 0.5$, and time $t = 10\,000$ (10 000 MC steps). The lines are as follows: (—) $p_b = 0.5$, (—■—) $p_b = 0.49$, (—□—) $p_b = 0.4$, (—▲—) $p_b = 0.2$, and (—◇—) $p_b = 0$.

applied frequency. We demonstrate here that under certain conditions the particle will undergo pure ballistic motion with a given velocity V . The condition is that $p_b = 1$, so that the alternating bias will enforce it to remain captured in a region between the origin and a distance h_r , which depends on the applied frequency $\nu = 1/2\tau$, so that

$$h_r = V\tau \quad (3)$$

Since the necessary condition is that $p^+ = 1$ (and thus $p^- = 0$) and vice versa during the next period, every single attempt will always be successful in the direction of the bias, that is, $V = 1$. On the other hand, if the bias is somewhat weaker than the limiting case, so that $p^+ \neq 1$, then there will always appear a diffusive component in addition to the ballistic drift. In this case, the particle will always propagate, albeit slowly, beyond h_r .

Figure 1 shows the fraction $f(h)$ of particles that propagate to a distance h under an alternating bias at a frequency $\nu = 0.02$ (this means that the bias alternates every $\tau = 25$ steps). The overall time of the calculation is $t = 10\,000$ steps. The jumps are performed using eq 2, where the jump probability is $p_{i,j} = 0.5$ modified by the factor p_b . The solid line is for bias probability $p_b = 0.5$, that is, $p^+ = 1$. There appears a sharp transition exactly at $h_r = 25$, as anticipated. It is seen from the figure that the span distance increases as the bias probability decreases.

The time development of the span distance in term of $f(h)$ is given in Figure 2. At short times, the concentration profile, $f(h)$, changes abruptly. The transition region broadens at longer times. For every curve, we denote as span distance $H(t)$ the position of the inflection point. Figure 3 illustrates the time dependence of $H(t)$ in log–log coordinates. The open points and solid line correspond to the case of no bias ($p_b = 0$), while solid points and dashed lines are for $p_b = 0.4$. Both curves are for a uniform probability $p_{i,j} = 0.5$.

Discussion

The straight solid line in Figure 3 indicates that, as expected, in the no bias case there is a pure random walk according to the equation

$$H = \sqrt{t} \quad (4)$$

If there is a bias, the situation becomes more complicated.

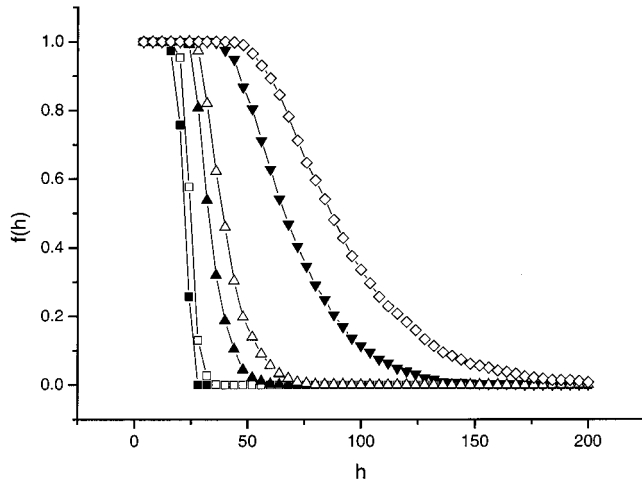


Figure 2. Concentration profiles (fraction $f(h)$) at different times. The frequency is $1/50$ ($\tau = 25$), $p_{ij} = 0.5$, and $p_b = 0.4$. The lines are as follows: (\blacksquare) $t = 25$, (\square) $t = 100$, (\blacktriangle) $t = 500$, (\triangle) $t = 1000$, (\blacktriangledown) $t = 5000$, and (\diamond) $t = 10\,000$.

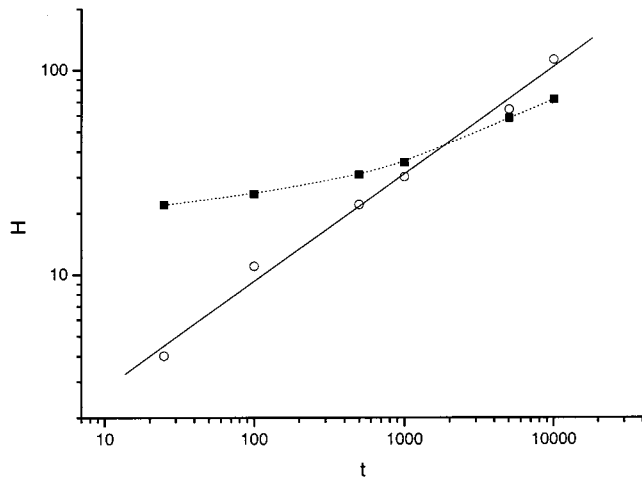


Figure 3. Penetration distance H . The frequency is $1/50$ ($\tau = 25$), $p_{ij} = 0.5$, and $p_b = 0.4$. The solid line and open points are for $p_b = 0$ (no bias, i.e., random walk). The solid points and dotted line are for $p_b = 0.4$.

There is a directed motion during the first period ($\tau = 25$), so that first point is $H(25) = 25$. During the next period, particles return almost to the origin. The diffusion drift is impinged very much by the directed motion.

As we already mentioned, the main idea is to find under which conditions the particle motion switches from a random walk to a pure ballistic one, so that particles will be forced to oscillate in the region around the origin and will never be permitted to penetrate inside the bulk of the system deeper than h . Figure 4 is an indication that this happens when the bias is so strong that $p^+ = 1$, as expected.

The same model can be interpreted in terms of activation energies assuming that the probabilities to jump follow Boltzmann statistics:

$$p_{ij} = \frac{1}{z} \exp(-E_{ij}) \quad (5)$$

where z is the coordination number (in a one-dimensional network $z = 2$) and E_{ij} is the height of the energy barrier in $k_b T$ units (k_b is the Boltzmann constant and T is the temperature). Varying the bias implies that the height of the barrier is changed by $\pm E_b$, the bias energy. The value of the activation energy barrier for diffusion varies usually

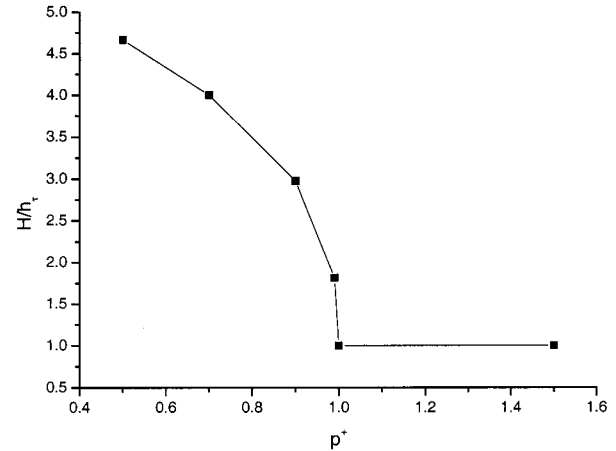


Figure 4. Dependence of dimensionless penetration distance H/h_{τ^+} on overall jump probability p^+ . The frequency is $1/50$ ($\tau = 25$), $p_{ij} = 0.5$, and time $t = 10\,000$ (10 000 MC steps).

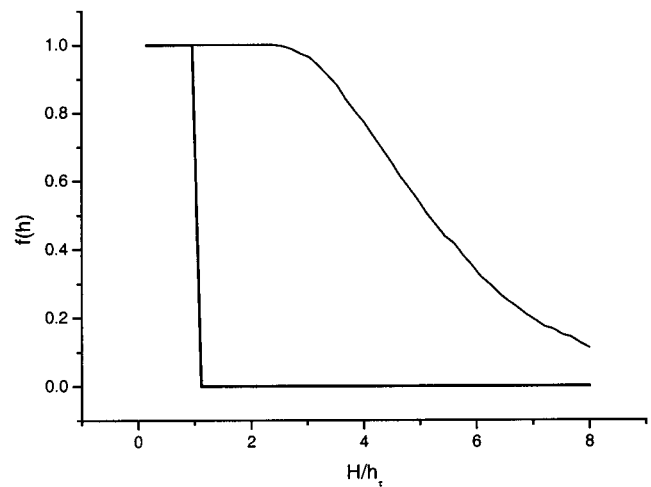


Figure 5. Concentration profiles (fraction $f(h)$) computed for $E_{ij} = 20$ and time $t = 10\,000\,000$. The frequency is $1/50$ ($\tau = 25$). The thick line is for $E_b = 20$, and the thin line is for $E_b = 19.9$. If $E_b > 20$, data always are on the thick line so that the particle cannot penetrate beyond h .

around 1 eV; that is, the value of E_{ij} varies between 20 and 40 (see for instance the temperature dependence of diffusion coefficients cited in ref 14). Under similar conditions, the jump probability is very low. In real systems, the time corresponding to one MC step is about 10^{-13} s (reverse of the vibration frequency of molecules). Therefore, one jump per second corresponds to $E_{ij} \approx 30$. For this reason, real systems are often modeled by MC programs in which every step is successful, but the time prescribed is determined by the Boltzmann formula. However, this approach is not capable of describing systems with an alternating bias. On the other hand, for $E_{ij} \approx E_b$ steps along the bias direction are permitted, so that the present algorithm is capable of following diffusion if the bias value is sufficiently high. Figure 5 shows the concentration profiles [fraction $f(h)$] computed for $E_{ij} = 20$ and time $t = 10^7$ MC steps. The frequency is $1/50$ ($\tau = 25$). The thick line is for $E_b = 20$, while the thin line is for $E_b = 19.9$. If $E_b > 20$, the data always are on top of the thick line. It is seen that motion has a catastrophic behavior: the particle cannot penetrate beyond h . It is important to note that the energy barrier to move opposite the bias direction remains sufficiently high.

The method of alternating bias offers several possibilities to separate particles. If there are two sorts of particles moving at different rates (V_1 and V_2), then a suitably chosen membrane of thickness L ($h_{r,1} < L < h_{r,2}$) will permit the penetration of faster moving particles 2 and stop particles 1. Another possibility is to vary the bias in such a way that, say, $p^{+(1)} = 1$ while $p^{+(2)} < 1$. In this case, particles 1 will not be able to penetrate a membrane of thickness L while slowly moving particles 2 will diffuse through it. For instance, we predict that a suitably chosen membrane with an alternating field will keep hydrogen cations (H^+) in the vicinity of a cathode while larger ions could move in the electrolyte.

Conclusions

The present computer model demonstrates that there are conditions under which motion switches from a random walk to a pure ballistic one, so that particles will be forced to oscillate in the region around the origin and will never be permitted to penetrate deeper into the system. Therefore, a high-frequency/high-energy alternating bias could serve as a protecting shield against some fast-moving species and at the same time permit a diffusive penetration of slower particles.

In the present work, we used a one-dimensional lattice as the simplest representation of a network. However, it is our belief that qualitatively similar results will be observed on any dimensionality lattice. Preliminary results on two-dimensional and three-dimensional lattices support this assumption. Despite their diversity, most networks appearing in nature follow universal organizing principles. Therefore, our approach is not limited to electrophoreses or to the penetration of ions through membranes. The properties of many systems can be described with properly chosen networks. We already mentioned many possible applications in the Introduction. For example, in sociology the present approach could be used to describe the spread of new ideas (in this case, the role of the alternating bias would be played by the economic situation).

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