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Ion Diffusion in a Coulombic Field

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An analytic solution of counter-ion diffusion in a semi-infinite domain near a uniformly charged surface is obtained within the Smoluchowski–Poisson–Boltzmann treatment. The long-ranged Coulombic interaction results in a finite first-passage time to the charged surface, although higher moments of the first-passage time are infinite. This problem is directly related to an exactly solvable model of a lattice random walk with a position-dependent bias.

KEY WORDS: Ion diffusion; random walks; first-passage times.

1. INTRODUCTION

We consider the diffusion of an assembly of identical point charges confined to the half-space $z > 0$. The system is neutralized by a plane of uniform charge located at $z = 0$ with surface charge density σ. The medium in $z > 0$ is treated as a continuum characterized by a dielectric constant ε, and the ions have a constant diffusion coefficient D in this medium. The dynamics of ion diffusion is treated in the Smoluchowski–Poisson–Boltzmann approximation in which the ions are considered to diffuse in an *external* field. As a consequence, dynamical ion–ion correlations are neglected. Furthermore, this external field is taken to be the equilibrium singlet potential of mean force given by the Poisson–Boltzmann theory[(1)] for Coulombic systems. The physical approximations behind this treatment of diffusion in Coulombic systems are discussed in detail elsewhere.[(2)] This model has been used to analyze ion diffusion in different geometries and ionic compositions[(3,4)] and the results compare favorably with stochastic dynamics simulations.[(5)]

For diffusion or random walks in infinite or semi-infinite domains, the first-passage times are in general infinite, as the diffuser has the propensity

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to "wander off to infinity." This divergence of the first-passage time can be overcome in semi-infinite domains by imposing a constant bias toward the boundary surface. For the problem considered in this paper, there is a bias toward the surface due to the long-ranged Coulombic interactions together with the absence of screening effects due to mobile charges of opposite signs. This bias is not constant. It decays with distance from the surface, but its decay is slow enough that the mean first-passage time to the surface is finite, although higher moments of the first-passage time diverge. These results are elucidated by noting the correspondence between the present ion diffusion problem and a related problem of lattice random walk in an external field.[6,7]

2. THE POISSON–BOLTZMANN PROBLEM

We first determine the equilibrium singlet potential of mean force according to the Poisson–Boltzmann theory for a negatively charged plane wall adjacent to an electrolyte consisting only of positive ions of a single species. Without loss of generality, we choose the electrostatic potential $\psi(z)$ to be zero at the negatively charged surface (where there is a uniform surface charge density $\sigma<0$) so that

$$\psi(z)=0 \qquad \text{at} \quad z=0 \tag{1}$$

and $\psi(z)>0$ for $z>0$. The Poisson–Boltzmann equation for $\psi(z)$ then reads

$$\psi''(z)=-(4\pi e n_0/\varepsilon)\exp[-\beta e\psi(z)] \tag{2}$$

where, in the Gaussian units employed, e (>0) is the charge on the ions, ε is the dielectric constant, and $\beta=1/(kT)$, with k denoting Boltzmann's constant and T the absolute temperature. The number density n_0 of ions at the surface is a constant to be determined. We introduce the variables

$$\kappa^2=8\pi n_0\beta e^2/\varepsilon \tag{3}$$

and

$$y(z)=\beta e\psi(z) \tag{4}$$

where y is the dimensionless electrostatic potential and κ is the screening parameter. (In this continuum treatment of the problem, the only length scale present is $1/\kappa$, the classical Debye length.) Equation (2) becomes

$$y''(z)=-(1/2)\kappa^2\exp[-y(z)] \tag{5}$$

The first integral of this equation is

$$[y'(z)]^2 = \kappa^2 \exp[-y(z)] \tag{6}$$

where the constant of integration is zero because the electric field $-\psi'(z)$ must vanish as $z \to \infty$; and from Eq. (6) this also implies that the potential $\psi(z) \to \infty$ in the same limit.

The surface concentration n_0 and hence the screening parameter κ can be determined from the boundary condition at $z = 0$:

$$\left.\frac{d\psi}{dz}\right|_{z=0} = -\frac{4\pi\sigma}{\varepsilon} \tag{7}$$

From Eqs. (1)–(6) this gives

$$\kappa^2 = 8\pi n_0 \beta e^2/\varepsilon = (4\pi\beta e\,|\sigma|/\varepsilon)^2 \tag{8}$$

A further integration of Eq. (6) gives

$$y(z) = \ln[(\kappa z + 2)^2/4] \tag{9}$$

and we see that unlike the classical plasma problem, in which the potential distribution is screened exponentially,[1] the reduced potential in this problem diverges logarithmically in the limit $z \to \infty$. The charge density in the electrolyte is given by $en_0 \exp[-y(z)] = 4en_0/(\kappa z + 2)^2$. Integrating this expression over z from 0 to ∞, we find a total electrolyte charge $|\sigma|$ per unit wall area, exactly balancing the charge on the wall.

3. THE SMOLUCHOWSKI–POISSON–BOLTZMANN PROBLEM

If a tagged ion diffuses in an external field with potential $w(\mathbf{r})$, the probability density $f(\mathbf{r}, t)$ for the position $\mathbf{r}$ of the tagged ion at time t obeys the Smoluchowski equation

$$\frac{\partial f(\mathbf{r}, t)}{\partial t} = D\,\nabla \cdot \{[\nabla + \beta\,\nabla w(\mathbf{r})]\, f(\mathbf{r}, t)\} \tag{10}$$

In the Smoluchowski–Poisson–Boltzmann (SPB) theory $w(\mathbf{r})$ is approximated by the product of the charge and the potential $\psi(z)$:

$$\beta w(\mathbf{r}) = \beta e\psi(z) = y(z) \tag{11}$$

Details of this theory as well as the approximations involved are discussed in detail elsewhere.[2] Since $w(\mathbf{r})$ is only a function of the normal coordinate z, diffusion in the directions parallel to the charged surface is simply free diffusion. If we write $\boldsymbol{\rho} = (x, y)$ and take the initial location of the tagged ion as $(0, 0, z_0)$, so that

$$f(\mathbf{r}, 0) = \delta(\boldsymbol{\rho})\, \delta(z - z_0) \tag{12}$$

we have

$$f(\mathbf{r}, t) = \frac{\exp(-\boldsymbol{\rho}^2/4Dt)}{4\pi\, Dt} F(z, t) \tag{13}$$

where $F(z, t)$ is the transverse-averaged propagator

$$F(z, t) = \int d^2\boldsymbol{\rho}\, f(\mathbf{r}, t) \tag{14}$$

We now introduce the dimensionless variables

$$\xi = \kappa z \tag{15}$$

$$\tau = \kappa^2\, Dt \tag{16}$$

$$\phi(\xi, t) = \kappa^{-1} F(z, t) \tag{17}$$

$$u(\xi) = y(z) \tag{18}$$

so that Eq. (10) becomes

$$\frac{\partial^2 \phi}{\partial \xi^2} + \frac{du}{d\xi}\frac{\partial \phi}{\partial \xi} + \frac{d^2 u}{d\xi^2}\phi = \frac{\partial \phi}{\partial \tau} \tag{19}$$

In terms of the dimensionless variables, with $\xi_0 \equiv \kappa z_0$, the initial condition on the dimensionless transverse-averaged propagator ϕ becomes

$$\phi(\xi, 0) = \delta(\xi - \xi_0) \tag{20}$$

We proceed by taking the Laplace transform of Eq. (19), writing

$$\tilde{\phi}(\xi, s) = \int_0^\infty d\tau\, \phi(\xi, \tau) \exp(-s\tau) \tag{21}$$

In terms of the new function $v(\xi)$ (which has its dependence on the Laplace variable s supressed), defined by

$$\tilde{\phi}(\xi, s) = v(\xi) \exp[-u(\xi)/2] \tag{22}$$

Eq. (19) becomes

$$v''(\xi) - \left\{ s + \frac{1}{2}\exp[-u(\xi)] \right\} v(\xi) = -\exp[u(\xi_0)/2]\, \delta(\xi - \xi_0) \tag{23}$$

[To reduce the differential equation to this simple form, one uses the dimensionless versions of Eqs. (5) and (6) to eliminate the derivatives of $u(\xi)$.] The two independent solutions of the homogeneous equation are

$$v_<(\xi) = [E(\xi) - 2s^{1/2}] \exp(+s^{1/2}\xi) \tag{24}$$

$$v_>(\xi) = [E(\xi) + 2s^{1/2}] \exp(-s^{1/2}\xi) \tag{25}$$

where

$$E(\xi) = \exp[-u(\xi)/2] \tag{26}$$

and the corresponding Wronskian is

$$W = v_< v'_> - v'_< v_> = 8s^{3/2} \tag{27}$$

Thus, the general solution of Eq. (23) which vanishes as $z \to \infty$ is

$$v(\xi) = -\exp[u(\xi_0)/2][v_<(\xi_<)\, v_>(\xi_>)/W] + \bar{A} v_>(\xi) \tag{28}$$

where

$$\xi_< = \min(\xi, \xi_0), \qquad \xi_> = \max(\xi, \xi_0) \tag{29}$$

The constant $\bar{A}$ in Eq. (28) has to be determined by the boundary conditions at the charged surface at $z = 0$. We can write Eq. (28) out in detail as

$$v(\xi) = \frac{\exp(-s^{1/2}\,|\xi - \xi_0|)}{8s^{3/2}E(\xi_0)} [4s - E(\xi_0)\, E(\xi) - 2s^{1/2}\, |E(\xi) - E(\xi_0)|]$$
$$+ A\, \frac{\exp[-s^{1/2}(\xi + \xi_0)]}{8s^{3/2}E(\xi_0)} [E(\xi_0) + 2s^{1/2}][E(\xi) + 2s^{1/2}] \tag{30}$$

where we have redefined the arbitrary constant to simplify subsequent algebra. The new arbitrary constant A again has to be determined by the boundary conditions at the charged surface at $z = 0$.

3.1. Absorbing Boundary

For an absorbing boundary we have $f(\mathbf{r}, t) = 0$ at $z = 0$, that is, $v(\xi) = 0$ at $\xi = 0$. Applying this to the general solution given by Eq. (30), we find

$$A = \frac{1 - 2s^{1/2}}{1 + 2s^{1/2}} \tag{31}$$

and the dimensionless transverse-averaged propagator $\phi(\xi, \tau)$ can be found by the inverse Laplace transform

$$\phi(\xi, \tau) = \frac{1}{2\pi i} \int_{c - i\infty}^{c + i\infty} ds\, \tilde{\phi}(\xi, s) \exp(s\tau) \tag{32}$$

Write for brevity

$$E = E(\xi) = 2/(\xi + 2), \qquad E_0 = E(\xi_0) = 2/(\xi_0 + 2) \tag{33}$$

The contour integral becomes

$$\phi(\xi, \tau) = \frac{E}{16\pi i E_0} \int_{c - i\infty}^{c + i\infty} ds \frac{\exp(s\tau)}{s^{3/2}} \Big\{ \exp(-s^{1/2} |\xi - \xi_0|) \times (4s - E_0 E - 2s^{1/2} |E - E_0|) + \exp[-s^{1/2}(\xi + \xi_0)] \frac{1 - 2s^{1/2}}{1 + 2s^{1/2}} \times (E_0 + 2s^{1/2})(E + 2s^{1/2}) \Big\} \tag{34}$$

The only singularity of the integrand in Eq. (34) in the complex s-plane is a branch cut along the negative real axis. By deforming the inversion contour to wrap around this branch cut, we have

$$\begin{aligned} \phi(\xi, \tau) = \frac{E}{8\pi E_0} \int_0^\infty d\zeta \frac{\exp(-\zeta\tau)}{\zeta^{3/2}} \times \Big\{ & (4\zeta + E_0 E) \cos[\zeta^{1/2}(\xi + \xi_0)] - 2\zeta^{1/2}(E - E_0) \sin[\zeta^{1/2}(\xi - \xi_0)] \\ & - \frac{\cos[\zeta^{1/2}(\xi + \xi_0)]}{4\zeta + 1} [(4\zeta + E_0)(4\zeta + E) - 4\zeta(E_0 + 1)(E + 1)] \\ & + \frac{2\zeta^{1/2} \sin[\zeta^{1/2}(\xi + \xi_0)]}{4\zeta + 1} [(E - 1)(4\zeta + E_0) + (E_0 - 1)(4\zeta + E)] \Big\} \end{aligned} \tag{35}$$

This is the final expression for the dimensionless transverse-averaged propagator $\phi(\xi, \tau)$ for an absorbing boundary at the surface $z = 0$.

3.2. Reflecting Boundary

At a reflecting boundary the normal component of the probability flux $\mathbf{J} = \nabla f + \beta(\nabla w) f$ vanishes at the surface ($z = 0$). In terms of the dimensionless function $v(\xi)$ defined by Eq. (22), this condition reduces to

$$\frac{dv}{d\xi} + \frac{1}{2} E(\xi)\, v(\xi) = 0 \tag{36}$$

at $\xi=0$. Applying this to the general solution given by Eq. (30), we find that the arbitrary constant A is unity. As with the absorbing boundary problem, the only singularity in the inverse Laplace transform integral is the branch cut along the negative axis of the complex s-plane. Consequently, the dimensionless transverse-averaged propagator $\phi(\xi, \tau)$ can be expressed as

$$\phi(\xi,\tau)=\frac{E}{8\pi E_0}\int_0^\infty d\zeta\,\frac{\exp(-\zeta\tau)}{\zeta^{3/2}} \times\{(4\zeta+E_0E)\cos[\zeta^{1/2}(\xi-\xi_0)]-2\zeta^{1/2}(E-E_0)\sin[\zeta^{1/2}(\xi-\xi_0)] + (4\zeta-E_0E)\cos[\zeta^{1/2}(\xi+\xi_0)]-2\zeta^{1/2}(E+E_0)\sin[\zeta^{1/2}(\xi+\xi_0)]\} \tag{37}$$

where E and E_0 are defined by Eq. (33).

3.3. Results

Figures 1 and 2 show examples of the dimensionless probability density function $\phi(\xi, \tau)$ for absorbing and reflecting boundary conditions at the surface. In both cases the initial position of the tagged ion is at $\xi_0=\kappa z_0=1$. In our Smoluchowski–Poisson–Boltzmann treatment of ions

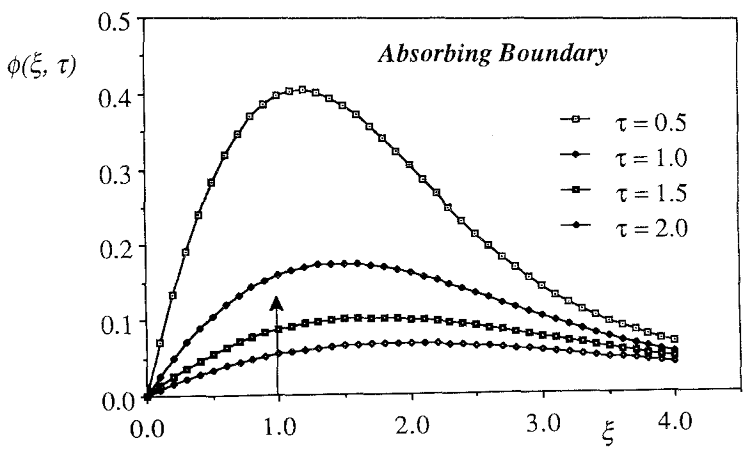

Fig. 1. The dimensionless probability density function $\phi(\xi, \tau)$ of a tagged ion as a function of the scaled distance $\xi=\kappa z$ for various values of the dimensionless time $\tau=\kappa^2 Dt$. The *absorbing boundary condition* is applied at the surface $z=0$. The initial position of the ion is at $\xi_0=\kappa z_0=1$; this is indicated by the arrow.

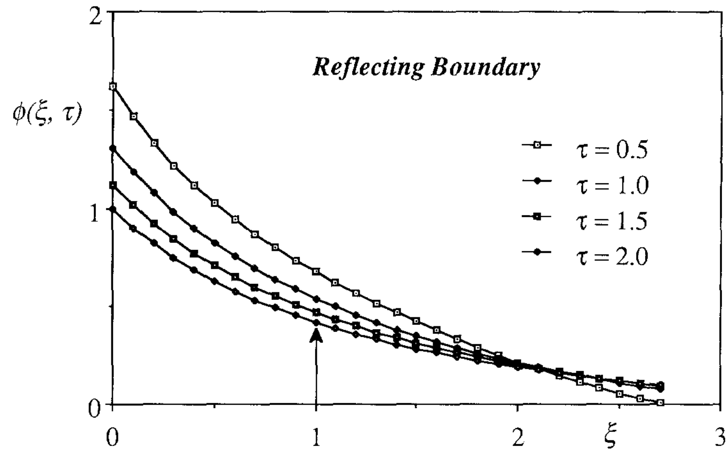

Fig. 2. The dimensionless probability density function $\phi(\xi, \tau)$ of a tagged ion as a function of the scaled distance $\xi = \kappa z$ for various values of the dimensionless time $\tau = \kappa^2 Dt$. The *reflecting boundary condition* is applied at the surface $z = 0$. The initial position of the ion is at $\xi_0 = \kappa z_0 = 1$; this is indicated by the arrow.

of a single sign diffusing in $0 < z < \infty$ (neutralized by a uniform surface charge at $z = 0$) the dimensionless probability density functions $\phi(\xi, \tau)$ given by Eqs. (35) and (37) are independent of the valence of the ions. From the results we see that the probability density of the tagged ion attains a quasiequilibrium distribution very rapidly and then slowly decays to zero via absorption at the surface for the absorbing boundary condition, and via "leakage" to infinity for both absorbing and reflecting boundary conditions.

4. THE FIRST-PASSAGE-TIME PROBLEM

In a diffusion process, the *mean first passage time* $T_1(z_1, z_0)$ from the plane $z = z_0$ to the plane $z = z_1$ is the mean time taken for a tagged particle departing from the plane $z = z_0$ to first reach the plane $z = z_1$ ($< z_0$). For diffusion governed by the Smoluchowski equation (10), with the potential w a function only of the coordinate z, this mean first passage time is given by the double integral[8,9]

$$T_1(z_1, z_0) = \frac{1}{D} \int_{z_0}^{z_1} dz \exp[\beta w(z)] \int_{\infty}^{z_1} dz' \exp[-\beta w(z')] \qquad (38)$$

For cases in which the external potential $w(z)$ is of finite range, the mean first-passage time $T_1(z_1, z_0)$ is infinite for diffusion in the infinite domain

$0 < z < \infty$. However, for the present problem of ions in the half-space $z > 0$ bounded by a neutralizing uniform surface charge density on the plane $z = 0$, $w(z)$ is of infinite range. It diverges logarithmically [see Eqs. (9) and (11)], so that

$$\exp[-\beta w(z)] = 4/(\kappa z + 2)^2 \tag{39}$$

Hence, the mean first-passage time is given explicitly by

$$T_1(z_1, z_0) = \frac{1}{2\kappa D}\,[(\kappa z_0 + 2)^2 - (\kappa z_1 + 2)^2] \tag{40}$$

and in particular, the *mean time of first arrival at the surface*

$$T_1(0, z_0) = \frac{1}{2\kappa D}\,[(\kappa z_0 + 2)^2 - 4] \tag{41}$$

increases quadratically with the initial position z_0. It can be shown from Eq. (34) that the variance of the mean time of first return for this problem is infinite, but the algebra involved is rather lengthy.

5. A RELATED RANDOM WALK PROBLEM

It turns out that the problem considered here can be mapped to a one-dimensional random walk problem introduced by Gillis[6] and studied further by Hughes and Sahimi.[7] We begin by approximating the dimensionless diffusion equation (19) by finite differences by choosing a spatial step size $\Delta\xi$ and a temporal step size $\Delta\tau$ so that $2\Delta\tau/(\Delta\xi)^2 = 1$. We further replace time derivatives by forward differences and spatial derivatives by central differences. If we write

$$P_n(m) = \phi(m\,\Delta\xi, n\,\Delta\tau), \qquad m, n = 0, 1, 2, 3,... \tag{42}$$

we find that

$$P_{n+1}(m) = \frac{1}{2}\left[\left(1 + \frac{\Delta\xi}{m\,\Delta\xi + 2}\right) P_n(m+1) + \left(1 - \frac{\Delta\xi}{m\,\Delta\xi + 2}\right) P_n(m-1)\right] - \frac{2(\Delta\xi)^2\, P_n(m)}{(m\,\Delta\xi + 2)^2} \tag{43}$$

If we hold $\Delta\xi$ fixed, for large values of m, Eq. (43) reduces to

$$P_{n+1}(m) = \frac{1}{2}\left[\left(1 + \frac{1}{m-1}\right) P_n(m+1) + \left(1 - \frac{1}{m+1}\right) P_n(m-1)\right] \tag{44}$$

In deriving Eq. (44), we retained in the coefficients of the quantities $P_n(m)$ terms that are constant or asymptotically proportional to $1/m$, and we adjusted terms that are of higher order[2] to ensure that solutions of Eq. (44) have the properties that (i) $\sum_{m=-\infty}^{\infty} P_n(m) = \sum_{m=-\infty}^{\infty} P_0(m)$ and (ii) if $P_0(m) \geqslant 0$ for all m, then $P_n(m) \geqslant 0$ for all m for $n > 0$. Without loss of generality, we may take $\sum_{m=-\infty}^{\infty} P_0(m) = 1$, in which case Eq. (44) is the evolution equation for a one-dimensional lattice random walk:

$$P_{n+1}(m) = \sum_{m'} p(m \mid m')\, P_n(m') \tag{45}$$

where

$$p(m \mid m') = \frac{1}{2}\left[\left(1 + \frac{1}{m'}\right)\delta_{m,m'-1} + \left(1 - \frac{1}{m'}\right)\delta_{m,m'+1}\right] \tag{46}$$

is the probability that a walker currently at site m' next steps to site m. Solving Eq. (45) with initial condition

$$P_0(m) = \delta_{m,M} \tag{47}$$

and appropriate boundary conditions gives a discrete analogue of the continuum diffusion problem analyzed above.

A class of walks with a variable bias, of which the present problem is a special case, was introduced by Gillis.[(6)] He investigated the statistics of return to the starting site for a walk commencing at $m = 0$ and subject to the transition probability law

$$p(m \mid m') = \left(\frac{1}{2} + \frac{k}{m'}\right)\delta_{m,m'-1} + \left(\frac{1}{2} - \frac{k}{m'}\right)\delta_{m,m'+1}, \quad m' \neq 0 \tag{48}$$

where $-1/2 < k < 1/2$, and

$$p(m \mid 0) = \tfrac{1}{2}\delta_{m,-1} + \tfrac{1}{2}\delta_{m,1} \tag{49}$$

[2] To illustrate the derivation of Eq. (44), consider the coefficient of $P_n(m+1)$ in Eq. (43). We have

$$1 + \frac{\Delta\xi}{m\,\Delta\xi + 2} = 1 + \frac{1}{m} + O\left(\frac{1}{m^2}\right) = 1 + \frac{1}{m-1} + O\left(\frac{1}{m^2}\right)$$

The expressions in the middle and on the right are equivalent for large m. However, the one on the right must be chosen if the $O(1/m^2)$ terms are to be discarded without loss of conservation of probability. Not all discretizations of a continuum equation that conserves probability will yield a discrete equation that conserves probability!

Equation (46) corresponds to the case $k = 1/2$ in Gillis' problem. Hughes and Sahimi[7] solved Gillis' problem for a walker with initial condition (47) and with Eq. (49) replaced by

$$p(m \mid 0) = \delta_{m,1} \tag{50}$$

corresponding to a reflecting barrier at the origin. [In their analysis, Montroll's defect technique[10] is used to derive a first-order linear differential equation for the discrete Fourier transform of the site occupancy probability generating function.] It is found that the generating function for the probability of occupancy of the origin is

$$P(0 \mid M; \xi) = \sum_{n=0}^{\infty} P_n(m)\, \xi^n \tag{51}$$

$$= \frac{\xi^M \Gamma(M+1+2k)\, {}_2F_1((M+1)/2+k, M/2+1+k; M+1; \xi^2)}{2^M M!\, \Gamma(M+1+2k)\, {}_2F_1(1/2+k, k; 1; \xi^2)} \tag{52}$$

where ${}_2F_1$ denotes the usual hypergeometric function.[11] In the special case $k = 1/2$, the hypergeometric function can be evaluated in terms of elementary functions and we find that

$$P(0 \mid M; \xi) = \frac{M(1-\xi^2)^{1/2} + 1}{1-\xi^2} \left[\frac{1-(1-\xi^2)^{1/2}}{\xi} \right]^M \tag{53}$$

If the walker arrives at $m = 0$, it is in a sense trapped there, since from $m = 0$ it can only step to $m = 1$, from which site it is always forced to return immediately to $m = 0$. Let $F_n(0 \mid M)$ denote the first-passage time distribution from site M to the origin, i.e., the probability of arriving at $m = 0$ for the first time on the nth step, with $F_n(0 \mid M)$ having the generating function

$$F(0 \mid M; \xi) = \sum_{n=1}^{\infty} F_n(0 \mid M)\, \xi^n \tag{54}$$

It is easily shown by standard techniques from the theory of recurrent events[12] that for $M > 0$,

$$F(0 \mid M; \xi) = P(0 \mid M; \xi)/P(0 \mid 0; \xi) \tag{55}$$

[Although Eq. (55) is usually presented for translationally invariant walks,[12] it is not restricted to translationally invariant walks.[13,14]] Hence,

$$F(0 \mid M; \xi) = [M(1-\xi^2)^{1/2} + 1] \left[\frac{1-(1-\xi^2)^{1/2}}{\xi} \right]^M \tag{56}$$

$$= 1 + M^2(\xi - 1) + O([\xi - 1]^{3/2}) \quad \text{as} \quad \xi \to 1- \tag{57}$$

We may now investigate the key statistical properties of the random walk. The probability of ever reaching the origin of coordinates is

$$R(0 \mid M) = \lim_{\xi \to 1-} F(0 \mid M; \xi) = 1 \tag{58}$$

and the mean first-passage time to the origin of coordinates is

$$T_1(0 \mid M) = \lim_{\xi \to 1-} \frac{\partial}{\partial \xi} F(0 \mid M; \xi) = M^2 \tag{59}$$

We find the same quadratic dependence on the initial distance from the wall as was obtained for the continuum problem in Eq. (41). The mean-square first-passage time can be calculated from an appropriate combination of the first and second derivatives of the first-passage time generating function. We find that it is infinite for $M > 1$. The formulas from Hughes and Sahimi[(7)] used to obtain these results are derived with a reflecting barrier at the origin, but for the calculation of first-passage times to the origin, the choice of the transition probability $p(m \mid 0)$ from the origin is of no significance.

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