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Internal Configurations of Span-Constrained Random Walks

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The spans of a random walk on a simple cubic lattice are the sides of the smallest rectangular box with sides parallel to the coordinate axes that entirely contain the random walk. We consider the position, at dimensionless time τ, of a random walker constrained by a set of spans S. We show in one dimension that if $S^2 \gg 4\tau$, the random walker tends to be located at the extremities of the span, while in the contrary case the random walker is most likely to be found halfway between the extremities. This is true whether the single-step transition probabilities have a finite or an infinite variance, as is shown by example. In higher dimensions the position of the random walker in the direction of the largest span tends to lie at the span extremities, while the position in the direction of the smallest span tends to be in the middle.

KEY WORDS: Random walks; spans; polymer configurations; stable laws; Poisson transformation.

1. INTRODUCTION

The spans of a random walk are defined to be the sides of the smallest rectangular box with sides parallel to the coordinate axes that entirely contain the random walk. That is to say, the span in the x direction at a fixed time is the maximum x displacement of the random walker minus the minimum x displacement. There have been two sources of interest in spans: statistics, and a description of shape for polymer chains. The earliest analyses of spans were those by Daniels[(1)] and Feller.[(2)] Kuhn[(3)] and Rubin[(4)] discussed spans in the context of polymer chain statistics and Rubin and Mazur[(5)] used simulation to study the spans of excluded-volume random walks. Further applications to the configurations of polymer chains were made by Rubin,

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Mazur, and Weiss.[6,7] Recent extensions of the mathematical theory were made by Weiss and Rubin,[8] who discussed span statistics of random walks with infinite-variance transition probabilities, as well as span statistics of random walks in continuous time.

All of the theories so far described deal with what might be called the external dimensions of the random walk. An analysis of the configurations of an adsorbed polymer chain between two plates[9] suggests that the internal configurations of a span-constrained random walk are likewise of interest. There are at least two ways in which to characterize the configurations. The first and easier is in terms of the probability density of the position of the random walker at an arbitrary time, and the second is in terms of the average occupancy of a region within the span, that is, the expected fraction of time spent by the random walker in that region since the beginning of the walk. Both of these characterizations lead to the interesting conclusion that there is a qualitative difference between the distributions in the direction of the largest and smallest spans; and indeed in a single dimension if the span is fixed and the time is varied, the distributions change from a U shape to a bell shape.

In this paper we will use the simpler of the two functions mentioned above to illustrate the properties of internal coordinates for symmetric random walks taking place on a lattice in discrete time.

2. ANALYSIS

Let $p(\mathbf{j})$ denote the single-step transition probability for the random walk, i.e., $p(\mathbf{j})$ is the probability that a random walker will be displaced by amount j in a single step. Associated with $p(\mathbf{j})$ is the structure factor $\lambda(\boldsymbol{\varphi})$ defined by

$$\lambda(\boldsymbol{\varphi}) = \sum_{\mathbf{j}} p(\mathbf{j}) \cos(\mathbf{j}\cdot\boldsymbol{\varphi}) \tag{1}$$

where the last form is valid for symmetric walks. The n-step transition probability will be denoted by $U_n(\mathbf{r})$ and can be expressed in terms of $\lambda(\boldsymbol{\varphi})$ as

$$U_n(\mathbf{r}) = \frac{1}{(2\pi)^m} \int_{-\pi}^{\pi} \cdots \int \lambda^n(\boldsymbol{\varphi}) \cos(\mathbf{r}\cdot\boldsymbol{\varphi})\, d^m\boldsymbol{\varphi} \tag{2}$$

for an m-dimensional lattice and a random walker initially at the origin.[10]

Let us first calculate the probability distribution for the internal coordinate of a random walk in one dimension. For this purpose we can start with the position distribution when the random walk takes place between absorbing barriers at $r = -a$ and $r = b$. This probability, denoted by $U_n(r; -a, b|r_0)$, is the probability that the random walker is at point r at step n, given that its initial position was r_0. The probability that we are after can be expressed in terms of the $U_n(r; -a, b|r_0)$. The probability that the random walker is at r having hit the point b at least once, while moving between absorbing barriers at $-a$ and $b + 1$, is

$$U_n(r; -a, b + 1|r_0) - U_n(r; -a, b|r_0)$$

Hence the probability that the random walker is at r at step n, having reached $-a$ and $+b$ at least once, is (omitting, for simplicity, the arguments r_0 and r)

$$\begin{aligned} V_n(-a, b) &= U_n(-a - 1, b + 1) - [U_n(-a - 1, b) - U_n(-a, b)] \\ &\quad - [U_n(-a, b + 1) - U_n(-a, b)] - U_n(-a, b) \\ &= \Delta_a \Delta_b U_n(-a, b) \end{aligned} \tag{3}$$

where Δ_a and Δ_b are difference operators with respect to a and b, respectively. An asymptotic expression for $U_n(r; -a, b|r_0)$ valid in the limit $a + b \to \infty$ can be found by using an eigenvalue expansion. The result of this calculation, outlined in greater detail in the Appendix, is

$$\begin{aligned} U_n(r; -a, b|r_0) = \frac{1}{a + b} \sum_{l=-(a+b-1)}^{a+b-1} \lambda^n_{a+b-1}\left(\frac{\pi l}{a + b}\right) \\ \times \sin\frac{\pi l(r_0 + a)}{b + a} \sin\frac{\pi l(r + a)}{b + a} \end{aligned} \tag{4}$$

where

$$\lambda_{a+b}(\varphi) = \sum_{s=-(a+b-2)}^{a+b-2} p(s) \cos s\varphi \tag{5}$$

for symmetric walks. We will mainly be interested in the limit $a + b \to \infty$, in which case $\lambda_{a+b}(\varphi) \sim \lambda(\varphi)$, where $\lambda(\varphi)$ is the structure function defined in Eq. (1). We will use this approximation in the analysis to follow. Since the initial point r_0 is of no intrinsic interest, it is convenient to work instead with the expected number of random walkers at point r at step n summed over all starting points. This function is

$$\begin{aligned} Q_n(r; -a, b) &= \sum_{r_0=-a}^{b} U_n(r; -a, b|r_0) \\ &= \frac{1}{a + b} \sum_{|2l+1| \leqslant a+b} \lambda^n\left(\frac{\pi(2l + 1)}{a + b}\right) \\ &\quad \times \cot\frac{\pi(2l + 1)}{2(a + b)} \sin\frac{\pi(2l + 1)(r + a)}{b + a} \end{aligned} \tag{6}$$

We first derive the probability density function for the internal coordinate of a one-dimensional random walk in continuous space, using the quantities developed so far. In the lattice case let the span at step n be denoted by S and let $p_n(r|S)$ be the conditional probability that the internal coordinate is r at step n, given that the span is S. If we combine Eqs. (3), (4), and (6), setting for simplicity the extremes of the random walk at $a = 0$ and $b = S$, we find that

$$p_n(r|S) = \Delta_a\Delta_b Q_n(r; -a, b) \Big/ \sum_{r=-a}^{b} \Delta_a\Delta_b Q_n(r; -a, b) \tag{7}$$

Notice that the denominator is just the probability that the span at step n is equal to S,[7]

$$p_n(S) = \Delta_S^2\left\{\frac{1}{S}\sum_{|2l+1|\leq S}\lambda^n\left(\frac{\pi(2l+1)}{S}\right)\cot^2\frac{\pi(2l+1)}{2S}\right\} \tag{8}$$

The first case of interest is that of a random walk, for which the single-step jump probabilities have a finite variance:

$$\sum_{j=-\infty}^{\infty} j^2 p(j) < \infty$$

so that to lowest order in φ

$$\lambda^n(\varphi) = \exp[n \ln \lambda(\varphi)] \sim \exp(-n\sigma^2\varphi^2/2) \tag{9}$$

Hence, by an argument that has been reproduced many times,

$$U_n(r) \sim \frac{1}{(2\pi n\sigma^2)^{1/2}}\exp\left(-\frac{r^2}{2n\sigma^2}\right) \tag{10}$$

This allows us to approximate $Q_n(r; -a, b)$ by

$$Q_n(r; -a, b) \sim \frac{2}{\pi}\sum_{l=-\infty}^{\infty}\frac{\exp[-\pi^2\sigma^2(2l+1)^2 n/(2(a+b)^2)]}{2l+1} \times \sin\frac{\pi(2l+1)(r+a)}{b+a} \tag{11}$$

since for large n, $a + b$ (i.e., the span S) is $O(n^{1/2})$ with a probability that approaches one as $n \to \infty$. Furthermore, since $|a|$ and $|b|$ must individually be $O(n^{1/2})$, we can replace the differences in Eq. (7) by derivatives with respect to these variables. If we set $n\sigma^2 = \tau$ and make a Poisson transformation of Eq. (11), we find that

$$\begin{aligned} Q_\tau(r; -a, b) &= \sum_{l=-\infty}^{\infty}(-1)^l\left\{\Phi\left(\frac{r+a+l(a+b)}{(2\tau)^{1/2}}\right) + \Phi\left(\frac{r+a-l(a+b)}{(2\tau)^{1/2}}\right) - 1\right\} \\ &= 2\sum_{l=-\infty}^{\infty}(-1)^l\Phi\left(\frac{r+a+l(a+b)}{(2\tau)^{1/2}}\right) \end{aligned} \tag{12}$$

where $\Phi(x)$ is the error function defined by

$$\Phi(x) = (2\pi)^{-1/2} \int_{-\infty}^{x} \exp(-u^2/2)\, du \tag{13}$$

In order to plot results that are comparable, we will normalize the internal coordinate by setting $r = \theta S$, where $0 \leqslant \theta \leqslant 1$. The probability distribution $p_n(r|S)$ in Eq. (7) then becomes a probability density $p_\tau(\theta|S)$, which is given by

$$p_\tau(\theta|S) = \frac{S^2}{4\tau} \frac{\sum_{l=-\infty}^{\infty} (-1)^l l(l+1)(l+\theta) \exp[-(S^2/(4\tau))(l+\theta)^2]}{\sum_{l=-\infty}^{\infty} (-1)^l l^2 \exp(-S^2 l^2/(4\tau))} \tag{14}$$

As one might expect, S and τ appear only in the combination S^2/τ. In the limit $\tau/S^2 \to \infty$ one can show, by starting from Eq. (11), that

$$p_\infty(\theta) = \tfrac{1}{2}\pi \sin \pi\theta \tag{15}$$

Some curves of $p_\tau(\theta|S)$ as a function of θ are shown in Fig. 1 for different values of $\beta = S^2/(4\tau)$. For $\beta < 1$ the curves are bell-shaped and for

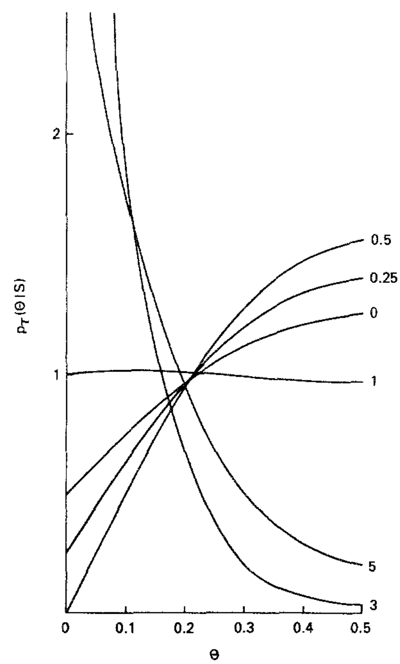

Fig. 1. Curves of $p_\tau(\theta|S)$ plotted as a function of θ for different values of the dimensionless parameter $S^2/(4\tau)$. Since $p_\tau(\theta|S)$ is symmetric around $\theta = 1/2$, the curves only extend from $\theta = 0$ to $\theta = 1/2$. This is true in the remaining figures as well.

larger values of β the curves are U-shaped. When β is close to 1 the normalized internal coordinate θ is distributed nearly uniformly in (0, 1). The qualitative picture that one gets is that when S is much greater than $\langle S\rangle$ at a fixed value of τ ($\langle S\rangle \approx 1.6\tau^{1/2}$) the random walker will tend to be found near the extremities of the span, while in the contrary case the random walker will be found mainly away from the extreme points. The function $p_\tau(\theta|S)$ is a conditional density. One can integrate over the span, provided that one starts with the joint probability for r and S, $p_\tau(r, S)$:

$$p_\tau(r, S) = \frac{1}{(4\pi\tau^3)^{1/2}} \sum_{l=-\infty}^{\infty} (-1)^{l+1} l(l+1)(r+lS) \exp\left[-\frac{1}{4\tau}(r+lS)^2\right] \tag{16}$$

which is normalized to unity. The probability density for θ will be denoted by $f(\theta)$ and is given by

$$f(\theta) = \int_0^\infty p_\tau(\theta S, S)S\,dS = \sum_{n=1}^{\infty} (-1)^{n+1}\left\{\frac{n(n+1)}{(n+\theta)^2} - \frac{n(n-1)}{(n-\theta)^2}\right\} \tag{17}$$

A curve of $f(\theta)$ as a function of σ is shown in Fig. 2, where it is seen that this averaged function is greatest near the extremities. If the average over S is

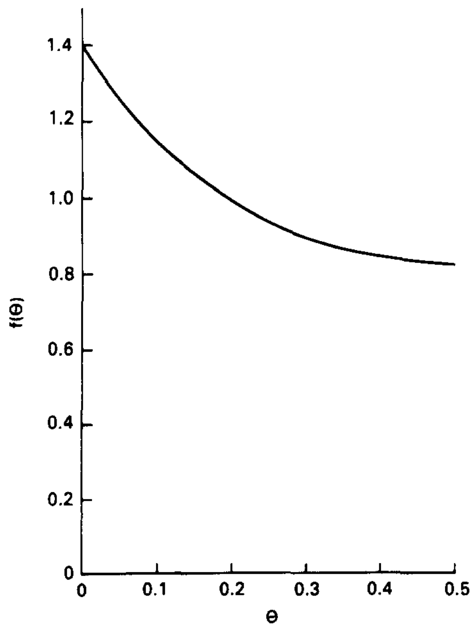

Fig. 2. The probability density for $f(\theta)$ averaged over all values of S as shown in (Eq. 17).

not taken to infinity but only to a finite upper limit, the resulting average can either be U-shaped or bell-shaped, depending on the parameter $\beta = S^2/\tau$.

So far we have considered only the case of jump probabilities that have a finite variance. When this condition is not satisfied, the approximation in Eq. (11) is not valid and the results will depend on specific details of how the sum

$$T_N = \sum_{j=-N}^{N} j^2 p(j) \tag{18}$$

diverges. Alternatively, one can say that the analog to Eq. (9) will depend on the behavior of $\lambda(\varphi)$ in the neighborhood of $\varphi = 0$. Some analysis can be given when $p(j) \sim Aj^{-2}$ for large $|j|$. For simplicity we consider only the case

$$p(j) = 3/(\pi^2 j^2), \qquad j = \pm 1, \pm 2, \pm 3, \ldots \tag{19}$$

for which

$$\lambda^n(\varphi) \sim \exp(-3n|\varphi|/\pi) \tag{20}$$

for small $|\varphi|$. In the limit of large n we can use Eq. (5) to show that

$$\begin{aligned} Q_n(r, -a, b) &\sim \frac{2}{\pi} \sum_{l=-\infty}^{\infty} \exp\left(-\frac{3n|2l+1|}{a+b}\right) \sin \pi(2l+1)\frac{r+a}{b+a}\frac{1}{2l+1} \\ &= \frac{2}{\pi} \sum_{l=-\infty}^{\infty} (-1)^l \tan^{-1}\left\{\frac{\pi}{3n}[r + a + l(a+b)]\right\} \end{aligned} \tag{21}$$

where the second line follows from the first by a Poisson transformation. If we use Eq. (7), we find for the conditional density for θ

$$p_n(\theta|S) \sim \frac{S}{3n}\sinh\left(\frac{3n}{S}\right) \sum_{l=-\infty}^{\infty} (-1)^{l+1} \frac{l(l+1)(l+\theta)}{[(l+\theta)^2 + (3n/(\pi S))^2]} \tag{22}$$

Some curves of $p_n(\theta|S)$ are shown in Fig. 3 plotted as a function of θ for different values of $\beta = S/(3n)$. A comparison of Figs. 1 and 3 shows that the behavior of the internal coordinate densities are qualitatively similar for both cases. One can show directly from Eq. (22) that $f(\theta)$, defined by the first line in Eq. (17), is the same as that found in the case of finite-variance transition probabilities. It is not clear whether this is true more generally.

Extension of the exact results to simple cubic lattices in higher numbers of dimensions is straightforward and we need not present it in detail. We have shown[8] that in the case of finite-variance transition probabilities the span distribution is asymptotically separable provided that the random walk is symmetric in each dimension. That is to say,

$$p_\tau(S_1, S_2, \ldots, S_n) \sim p_\tau^{(1)}(S_1) p_\tau^{(1)}(S_2) \cdots p_\tau^{(1)}(S_n)$$

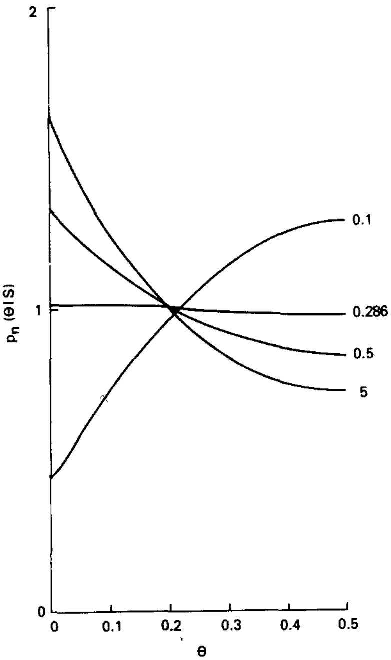

Fig. 3. Curves of $p_n(\theta|S)$ corresponding to a stable law whose single-step transition probabilities are $p(j) = (3/\pi^2)j^{-2}, j = \pm 1, \pm 2, \ldots$. The different curves correspond to different values of $S/3n$.

as $t \to \infty$, where $p_\tau^{(1)}(S)$ is the span density in one dimension. In this asymptotic regime the probability density of the internal coordinate of any span is identical to that found in the one-dimensional case. One can derive results analogous to that in Eq. (17) for ordered spans in k dimensions. If $P_\tau(S)$ is the probability that in (dimensionless) time τ a one-dimensional span is $\leqslant S$, then the probability densities for the internal coordinates of the smallest and largest spans, respectively, are

$$f_1(\theta) = k\int_0^\infty p_\tau(\theta S, S)[1 - P_\tau(S)]^{k-1}S\,dS$$

$$f_k(\theta) = k\int_0^\infty p_\tau(\theta S, S)P_\tau^{k-1}(S)S\,dS \tag{23}$$

The probability $P_\tau(S)$ is[8]

$$P_\tau(S) = \frac{8}{\pi^2}\sum_{n=0}^\infty \frac{1}{(2n+1)^2}\left[1 + \frac{\pi^2(2n+1)^2\tau}{S^2}\right]\exp\left(-\frac{\pi^2(2n+1)^2\tau}{S^2}\right) \tag{24}$$

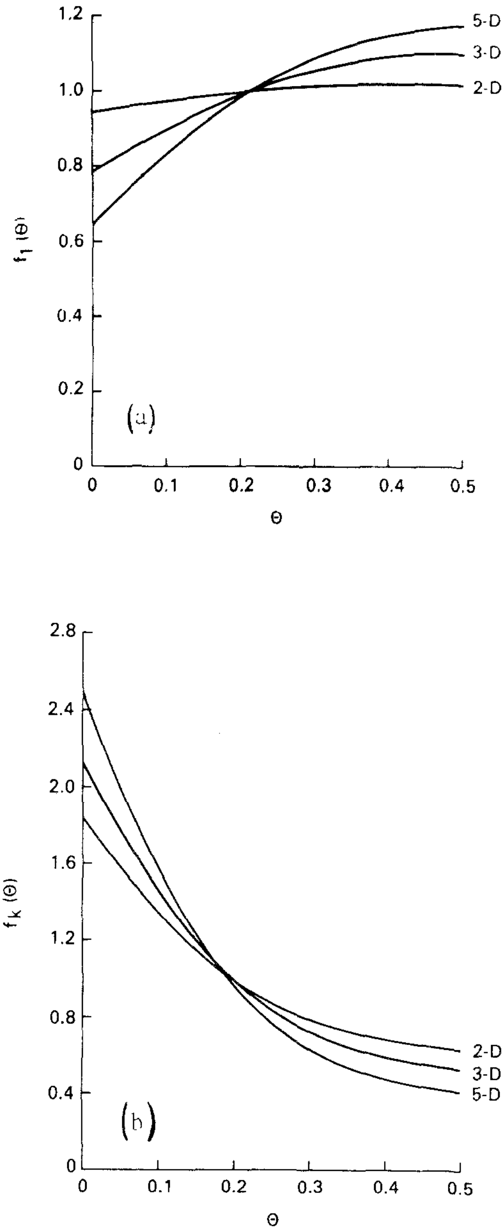

Fig. 4. (a) Curves of the probability density of $f_1(\theta)$ corresponding to the smallest ordered span in different numbers of dimensions. (b) The same for the largest ordered span.

Notice that $f_1(\theta)$ and $f_k(\theta)$ are independent of τ, as one can easily verify from the definitions of $p_\tau(r, S)$ and $P_\tau(S)$. Some curves of $f_1(\theta)$ and $f_k(\theta)$ as functions of θ are shown in Fig. 4. The curves indicate that in the direction corresponding to the largest span the random walker tends to be found nearer to the extremities of the span, while in the direction of the smallest span the random walker tends to be found closer to the central portion of the span. This asymmetry is accentuated as the number of dimensions increases. It was first observed by Rubin and Mazur[11] in recent simulation studies and is related to the asymmetries in random walks discussed by Kuhn,[12] Hollingsworth,[13] and others.[14,15]

Our results can be generalized in several directions. We started from a random walk in discrete time, but the formulas that arise from a continuous-time random walk[16] can be found quite simply. Let $\psi(t)$ be the probability density for the time between jumps and let $\psi^*(s)$ be the Laplace transform of $\psi(t)$. Then the Laplace transform of the time-dependent analog of $Q_n(r; -a, b)$ [Eq. (11)] is

$$Q_s^*(r; -a, b) = \frac{1 - \psi^*(s)}{s(a + b)} \times \sum_l \frac{\cot[\pi(2l + 1)/(2(a + b))] \sin[\pi(2l + 1)(r + a)/(a + b)]}{1 - \psi^*(s)\lambda(\pi(2l + 1)/(a + b))} \tag{25}$$

If the mean time between successive steps is $\mu < \infty$, then it follows from an analysis similar to that given in Ref. 8 that Eq. (14) remains valid at times $t \gg \mu$ provided that the parameter τ in that equation is defined by $\tau = \sigma^2 t/\mu$. A similar remark is true for Eq. (22), provided that n is replaced by t/μ. In a later study we will analyze further properties of span-constrained random walks suggested by the work of Dimarzio and Rubin.[9] These will include statistics of the occupancy, and the expected number of points visited in an n-step random walk.

APPENDIX. DERIVATION OF EQ. (4)

Without loss of generality we can consider a symmetric random walk confined to an interval $(1, N - 1)$ so that all lattice points $\geqslant N$ or $\leqslant 0$ are considered to be absorbing points. For simplicity we abbreviate $U_n(r; 0, N|r_0)$ by $U_n(r)$ since the barriers remain fixed in the calculation. It then follows that if $r \in (1, N - 1)$, the transition probabilities satisfy

$$U_{n+1}(r) = \sum_{\rho=1}^{N-1} U_n(\rho)p(r - \rho), \qquad U_0(r) = \delta_{r,r_0} \tag{A1}$$

In order to find an asymptotic solution we will assume that the solution can be represented as

$$U_n(r) = \sum_{j=1}^{N-1} A_j(n) \sin(\pi jr/N) \tag{A2}$$

and seek to find the $A_j(n)$. If we use the orthogonality relation

$$\sum_{r=1}^{N-1} \sin \frac{\pi jr}{N} \sin \frac{\pi j'r}{N} = \frac{N}{2} \delta_{j,j'} \tag{A3}$$

we find that the $A_j(n)$ satisfy

$$\begin{aligned} A_j(n+1) &= \frac{2}{N} \sum_{r=1}^{N-1} \sum_{\rho=1}^{N-1} \sum_{l=1}^{N-1} A_l(n) p(r-\rho) \sin \frac{\pi l\rho}{N} \sin \frac{\pi jr}{N} \\ &= \frac{2}{N} \sum_{l=1}^{N-1} A_l(n) \sum_{\rho=1}^{N-1} \sin \frac{\pi l\rho}{N} \sum_{s=1-\rho}^{N-1-\rho} p(s) \sin \frac{\pi l(\rho+s)}{N} \end{aligned} \tag{A4}$$

We can rewrite the innermost sum over s as

$$\sum_{s=1-\rho}^{N-1-\rho} = \sum_{s=-(N-2)}^{N-2} - \sum_{s=N-\rho}^{N-2} - \sum_{s=-(N-2)}^{-\rho} \tag{A5}$$

When we make this decomposition and take advantage of the orthogonality relation in Eq. (A3), we find that

$$\begin{aligned} A_j(n+1) = \lambda_{N-2}(j) A_j(n) &- \frac{2}{N} \sum_{l=1}^{N-1} A_l(n) \sum_{\rho=1}^{N-1} \sin \frac{\pi l\rho}{N} \\ &\times \left(\sum_{s=N-\rho}^{N-2} + \sum_{s=-(N-2)}^{-\rho} \right) p(s) \sin \frac{\pi j(\rho+s)}{N} \end{aligned} \tag{A6}$$

We will look for a recursive solution of the form

$$A_j(n) = A_j^{(0)}(n) + A_j^{(1)}(n) + A_j^{(2)}(n) + \cdots$$

where the zeroth order iterate is chosen to satisfy

$$A_j^{(0)}(n+1) = \lambda_{N-2}(j) A_j^{(0)}(n) \quad \text{or} \quad A_j^{(0)}(n) = \frac{2}{N} \sin\left(\frac{\pi jr_0}{N}\right) \lambda_{N-2}^n(j) \tag{A7}$$

Since this choice of the $A_j^{(0)}(0)$ assures us that the initial condition on the $U_0(r)$ is satisfied, we must also have $A_j^{(m)}(0) = 0$ for $m \neq 0$. In the next order of iteration we have

$$\begin{aligned} A_j^{(1)}(n+1) = \lambda_{N-2}(j) A_j^{(1)}(n) &\\ - \frac{4}{N^2} \sum_{l=1}^{N-1} \lambda_{N-2}^n(l) &\sum_{\rho=1}^{N-1} \sin \frac{\pi lr_0}{N} \sin \frac{\pi l\rho}{N} \sin \frac{\pi j\rho}{N} \\ &\times \left(\sum_{s=N-\rho}^{N-2} + \sum_{s=-(N-2)}^{-\rho} \right) p(s) \cos \frac{\pi js}{N} \end{aligned} \tag{A8}$$

Since the last term is a known quantity, at least in theory, we will call it $B_j(n)$. It is then easy to verify that a solution to this last equation is

$$A_j^{(1)}(n) = -(\lambda_{N-2}^{n}(j)B_j(0) + \lambda_{N-2}^{n-1}(j)B_j(1) + \lambda_{N-2}^{n-2}(j)B_j(2) + \cdots + B_j(n)) \tag{A9}$$

We therefore turn our attention to the $B_j(k)$, where

$$B_j(k) = \frac{4}{N^2}\sum_{l=1}^{N-1}\lambda_{N-2}^{k}(l)\sum_{\rho=1}^{N-1}\sin\frac{\pi l r_0}{N}\sin\frac{\pi l \rho}{N}\sin\frac{\pi j \rho}{N} \times\left(\sum_{s=N-\rho}^{N-2} + \sum_{s=-(N-2)}^{-\rho}\right)p(s)\cos\frac{\pi j s}{N} \tag{A10}$$

By summing over l we can also write this as

$$B_j(k) = \frac{2}{N}\sum_{\rho=1}^{N-1}U_k^{(0)}(\rho)\sin\left(\frac{\pi j\rho}{N}\right)\left(\sum_{s=N-\rho}^{N-2} + \sum_{s=-(N-2)}^{-\rho}\right)p(s)\cos\frac{\pi j s}{N} \tag{A11}$$

where

$$U_k^{(0)}(\rho) = \frac{2}{N}\sum_{l=1}^{N-1}\lambda_{N-2}^{k}(l)\sin\frac{\pi l\rho}{N}\sin\frac{\pi l r_0}{N} \tag{A12}$$

is the k-step transition probability in the zeroth order of iteration.

We will now show that $A_j^{(1)}(n)\to 0$ at a rate faster than $1/N$ as $N^2/(n\sigma^2)\to\infty$ for the case of symmetric, finite-variance random walks, by an approximate evaluation of the $B_j(n)$. A similar proof can be given for random walk characterized by the transition probability given in Eq. (19). In the limit $N^2/(n\sigma^2)\to\infty$ the asymptotic expression for $U_n^{(0)}(\rho)$ can be derived as

$$U_n^{(0)}(\rho) \approx \frac{1}{(2\pi n\sigma^2)^{1/2}}\left\{\exp\left[-\frac{(\rho - r_0)^2}{2n\sigma^2}\right] - \exp\left[-\frac{(\rho + r_0)^2}{2n\sigma^2}\right]\right\} \tag{A13}$$

by converting the sum to an integral. As a second step we would like to convert the sum over ρ in Eq. (A11) to an integral. For this purpose we will need to redefine the sums over s so that the limits are continuous variables rather than discrete ones. This can be done, for example, by defining the limit $N - \rho$ to be $[N - \rho]$ where the $[\cdots]$ means "largest integer contained in." Furthermore, we can set $\rho = Nv$ and $r_0 = N\theta$, where v is the integration variable and $\theta = O(1)$. We then find that

$$B_j(n) \sim \left(\frac{2}{\pi n\sigma^2}\right)^{1/2}\int_0^1\left\{\exp\left[-\frac{N^2}{2n\sigma^2}(v-\theta)^2\right] - \exp\left[-\frac{N^2}{2n\sigma^2}(v+\theta)^2\right]\right\} \times\sin(\pi j v)\left(\sum_{s=[N-Nv]}^{N} + \sum_{s=-N}^{[-Nv]}\right)p(s)\cos\frac{\pi j s}{N}\,dv \tag{A14}$$

Since $N^2/n\sigma^2$ is assumed to be large, we can use Laplace's method to find an approximate value of the integral. It is obvious that in that limit only the neighborhood of $v = \theta$ will lead to a contribution. It is straightforward to show that

$$B_j(n) \sim \frac{2}{N}\sin(\pi j\theta)\left(\sum_{s=[N(1-\theta)]}^{N} + \sum_{s=-N}^{[-N\theta]}\right)p(s)\cos\frac{\pi js}{N} \tag{A15}$$

But the sums in this expression are $o(1)$ as $N \to \infty$, so that $B_j(n) \sim \epsilon_j(N)/N$, where $\epsilon_j(N) \to 0$ as $N \to \infty$. Thus the $A_j^{(1)}(n)$ are asymptotic to

$$A_j^{(1)}(n) \sim -\frac{\epsilon_j(N)}{N}\frac{1-\lambda_{N-2}^{n+1}(j)}{1-\lambda_{N-2}(j)} \tag{A16}$$

which tends to zero at a rate faster than $1/N$ as $N \to \infty$. A similar argument can be used to show that when $m > 1$ the $A_j^{(m)}(n)$ tend to zero at an even faster rate as $N \to \infty$.

As a final step we can change the interval $(0, N)$ to $(-a, b)$ by changing ρ to $\rho + a$ and r_0 to $r_0 + a$ in Eq. (A12) and changing N to $a + b$. This leads to the result given in Eq. (4).

REFERENCES

1. H. E. Daniels, *Proc. Camb. Phil. Soc.* **37**:244 (1941).
2. W. Feller, *Ann. Math. Stat.* **22**:427 (1951).
3. H. Kuhn, *Experientia* **1**:28 (1945).
4. R. J. Rubin, *J. Chem. Phys.* **56**:5747 (1972).
5. R. J. Rubin and J. Mazur, *J. Chem. Phys.* **63**:5362 (1975).
6. R. J. Rubin, J. Mazur, and G. H. Weiss, *Pure Appl. Chem.* **46**:143 (1976).
7. R. J. Rubin and G. H. Weiss, *Macromol.* **10**:332 (1977).
8. G. H. Weiss and R. J. Rubin, *J. Stat. Phys.* **14**:333 (1976).
9. E. A. Dimarzio and R. J. Rubin, *J. Chem. Phys.* **55**:4318 (1971).
10. E. W. Montroll, *J. Soc. Ind. Appl. Math.* **4**:241 (1956).
11. R. J. Rubin and J. Mazur, *Macromol.* **10**:139 (1977).
12. W. Kuhn, *Koll. Z.* **68**:2 (1934).
13. C. Hollingsworth, *J. Chem. Phys.* **17**:97 (1949).
14. K. Solc and W. Stockmayer, *J. Chem. Phys.* **54**:2756 (1971).
15. K. Solc, *J. Chem. Phys.* **55**:335 (1971).
16. E. W. Montroll and G. H. Weiss, *J. Math. Phys.* **6**:167 (1965).