Crossover time of diffusion-limited reactions on a tubular lattice

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We studied the diffusion-limited reactions $A+A\rightarrow 0$ and $A+B\rightarrow 0$ and the number of distinct sites visited by a random walker on a d-dimensional tubular lattice: square lattice of sizes $L\times W^{d-1}$ with $L\gg W$. We are interested in the crossover time at which the system changes its behavior from that in high dimensions to that in one dimension. We analytically solved the random-walk problem on the tubular lattice. Our theoretical result agrees with the simulation and thus explains the anomalous scaling of the crossover time for the random-walk problem. We also understood, using the concept of depletion zone, the scaling behavior of the crossover time for the reaction $A+A\rightarrow 0$ on the tubular lattice. Our measurement and data collapse showed that the crossover time for the reaction $A+B\rightarrow 0$ scales as W^2 for large W. The discrepancy between our result and that of others is also discussed. [S1063-651X(97)07006-2]

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I. INTRODUCTION

The diffusion-limited reaction of particles on a hyperdimensional surface is a problem of fundamental interest and practical importance [1–6]. Simulation, theory, and experiments show that in low dimensions the diffusion-limited reaction no longer obeys the classical reaction rule. This is due to the effect of local concentration fluctuation in low dimensions. For bimolecular elementary reactions of the form $A+A\rightarrow 0$ it is well known that the critical dimension is 2, below which the concentration of reactant A decays, asymptotically, as $t^{-d/2}$. This nonclassical behavior is caused by the anomalously large and continuously growing depletion zones that are mesoscopic domains depleted of reactants [2,3]. For elementary reactions of the form $A+B\rightarrow 0$, the critical dimension is 4 and below that concentration of reactant decays as $t^{-d/4}$. An even more dramatic nonclassical effect has been shown for the reaction $A+B\rightarrow 0$ below dimension 4: Self-segregation between A and B appears for an initially random system [4–6].

It can be seen that the nonclassical behavior is most obvious in one dimension. While strictly one-dimensional reaction systems are difficult to realize, it is much easier to achieve systems that are effectively one dimension, for example, capillaries, pores, or tubules. Recently Lin, Kopelman, and Argyrakis [7] performed Monte Carlo simulations of random-walk-based exploration volumes and bimolecular $A+A\rightarrow 0$ and $A+B\rightarrow 0$ reactions on a tubular (they called it baguettelike) lattice. The d-dimensional tubular lattice has an infinitely long geometry in one (longitudinal) direction and finite width W in the remaining $d-1$ (transverse) directions. They investigated the crossover time of the system from high- (two- or three-) dimensional behavior to one-dimensional behavior and its scaling laws with respect to the tube width W. They found that these dimensional crossover times deviate significantly from a mean-square displacement law and are specific to both dimensionality and reaction type: Instead of being an expected power of 2, the exponents range between 1 and 4.

In this paper we analytically solved the random-walk problem on the tubular lattice. Using a simple intuitive argument, we also obtained the same result. Our theoretical result agrees with the simulation and thus successfully explains the crossover time of the random-walk problem. Therefore, we also understood, using the concept of depletion zone, the scaling behavior of the crossover time for the reaction $A+A\rightarrow 0$ on the tubular lattice. Our measurement and data collapse show that the crossover time for the reaction $A+B\rightarrow 0$ scales as W^2 for large W. The discrepancy between the result of Lin *et al.* and ours is also analyzed.

In Sec. II we define the model and specify the parameters and boundary conditions. In Sec. III we apply an intuitive argument to obtain the number of distinct sites visited by a random walker in a tubular geometry. Using the analytical results, we are able to explain the abnormal scaling of the crossover time for the random-walk problem and the $A+A\rightarrow 0$ reaction. In Sec. IV we employ different methods to measure the scaling exponent of the crossover time for the reaction $A+B\rightarrow 0$. Diffusion-reaction equations are used to explain the result. Finally, in Sec. V we discuss the difference between the result of Lin *et al.* and ours. In the Appendixes we give the rigorous derivation of the formula obtained in Sec. III.

II. MODEL

The method of simulation we employed is essentially the same as that of Lin *et al.* [7]. For clarity and consistency we briefly reiterate the procedure as follows: A population of reacting particles is initially deposited on a tubular lattice: The linear size L of the lattice in one direction (longitudinal) is much larger than that (W) of the others (transverse). Particles move by hopping on the lattice and react when they encounter each other. For the $A+A\rightarrow 0$ type reaction, if two A particles attempt to occupy the same lattice site they annihilate each other. The $A+B\rightarrow 0$ type reaction occurs when an A and a B particle attempt to occupy the same lattice site. No reaction happens if two same-species particles ''collide'' and therefore each lattice site can hold at most one particle. Periodic boundary conditions are applied in both cases and the density $\rho_A(t)$ of reactant A is kept track of. For the random-walk problem one random walker is released at time

$t=0$ from the origin and S_t, the number of distinct sites visited by the walker, is recorded. Here the linear size along the longitudinal direction is infinite and periodic boundary conditions are applied along the transverse directions. In all three cases we are interested in the crossover time, defined as the point at which the system changes its behavior from that in two or three dimensions to that in one dimension.

III. CROSSOVER TIME OF S_t

Because of the translational invariance symmetry in the random-walk problem we can solve, using the generating function technique [8], the asymptotic behavior of S_t on the tubular lattice. We postpone the rigorous derivation until the Appendixes and instead present a much simpler point of view here, which can be applied to the case of periodic boundary conditions along the transverse directions as well as that of reflective boundary conditions.

We start from the well-known [8] fact that in one-dimensional free space the number of distinct sites visited by a random walker as a function of time t is, asymptotically,

$$S_t \sim \sigma \sqrt{\frac{8t}{\pi}}, \tag{1}$$

where σ is the single-step dispersion. The walker spends approximately $\sqrt{t}$ time (we call it ''idle'' time) visiting two consequent *newly* visited sites. In the tubular lattice, if we just concentrate on the longitudinal direction, say, by projecting the d-dimensional motion into that direction, the number of distinct *layers* visited by the walker is $\sigma\sqrt{8t/\pi}$, with $\sigma^2=1/2d+1/2d=1/d$. During the ''idle time'' the walker will just visit (almost) all the sites on the transverse constrained hyperplanes (layers) because of the finite size of the hyperplanes. This can also be confirmed by simulation results. Therefore, the number of distinct *sites* visited by a random walker on the tube is, asymptotically,

$$S_t \sim \sigma \sqrt{\frac{8t}{\pi}} W^{d-1} = \sqrt{\frac{8t}{\pi d}} W^{d-1}, \tag{2}$$

where W is the linear size of the tubular lattice along the transverse directions and d the embedding dimension.

It is also well known [8] that in two- or three-dimensional free space the number S_t of distinct sites visited by a random walker as a function of time t is, asymptotically,

$$S_t \sim \begin{cases} \dfrac{t}{\ln(t)} & \text{for} \quad d=2 \\ t & \text{for} \quad d=3. \end{cases} \tag{3}$$

Therefore, according to Eqs. (2) and (3) the crossover time t_c from $(d=3)$-dimensional behavior to $(d=1)$-dimensional behavior can be obtained by solving the equation $t_c \sim \sqrt{t_c} W^2$, which gives the scaling relationship between t_c and W,

$$t_c \sim W^4. \tag{4}$$

The scaling power 4 agrees with the simulation result obtained in [7]. Similarly, the crossover time t_c from $(d=2)$-dimensional behavior to $(d=1)$-dimensional behavior is just the solution of $t_c/\ln t_c \sim \sqrt{t_c} W$ or

$$\frac{\sqrt{t_c}}{\ln\sqrt{t_c}} \sim W, \tag{5}$$

which has no simple global scaling behavior. The scaling exponent (2.6 ± 0.4) observed in [7] is the property of the local solution. Furthermore, for large W and thus large t_c, $\ln t_c$ can be treated as constant compared to t_c and therefore t_c approaches the classical scaling relationship $t_c \sim W^2$.

IV. CROSSOVER TIME OF $A+A\rightarrow 0$ AND $A+B\rightarrow 0$

In diffusion-reaction systems, such as $A+A\rightarrow 0$ or $A+B\rightarrow 0$, one is usually interested in the density of the reactants ρ_A (and/or ρ_B). Thus, in such systems the crossover time can be defined as the point at which the density changes its behavior from that in two or three dimensions to that in one dimension. Had the reaction process behaved classically, the density, say ρ_A, would have followed the asymptotic form $\rho_A \sim t^{-1}$, which is independent of the spatial dimension the system embedded in and therefore there would have been no crossover. For the reaction $A+A\rightarrow 0$ in free space, the concentration decay rate can be understood using the concept of depletion zone [1,9]: As a first-order approximation, in the area swept by a surviving particle up to time t, there is only one particle, i.e., the surviving particle. This argument gives $\rho_A(t) \sim 1/S_t$, where $\rho_A(t)$ is the density of particle A at time t. Motivated by the result obtained in Sec. III, one would assume that the density ρ_A of the reaction system $A+A\rightarrow 0$ on the tubular lattice follows, asymptotically,

$$\rho_A^{-1} \sim W^{\beta} t^{1/2} \tag{6}$$

and the exponent $\beta=d-1$ as in the random-walk problem. This argument explains the same scaling exponent of the crossover time for both the random-walk problem and the reaction $A+A\rightarrow 0$ [7].

Similarly, one would expect that the temporal behavior of ρ_A, for the reaction $A+B\rightarrow 0$ and $d<4$, on the tubular lattice follows (assume initially $\rho_A=\rho_B$)

$$\rho_A^{-1} \sim \begin{cases} t^{d/4} & \text{for small} \quad t \\ W^{\beta} t^{1/4} & \text{for large} \quad t. \end{cases} \tag{7}$$

The rate $\rho_A^{-1} \sim t^{d/4}$ is the nonclassical (Ovchinnikov-Zeldovich) asymptotic behavior [4–6] of the reaction $A+B\rightarrow 0$ in d-dimensional free space and therefore the early time behavior in Eq. (7) is true only in the sense of large enough width W. In real simulations (usually W cannot be very large) a finite-size effect sets in before one can see the d-dimensional Ovchinnikov-Zeldovich rate $\rho_A^{-1} \sim t^{d/4}$. In real simulations there is also another finite-size effect, namely, along the longitudinal direction. Since the size along the longitudinal direction is set large enough in the simulation, the one-dimensional behavior can be observed before the longitudinal finite size has an effect.

The crossover of the reaction $A+B\rightarrow 0$ occurs at the point

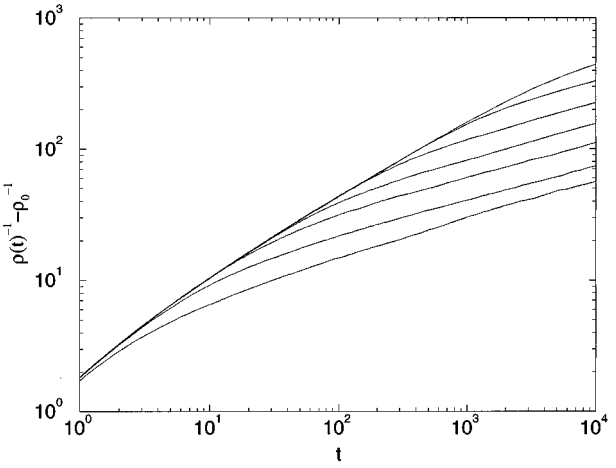

FIG. 1. Concentration $\rho(t)^{-1}-\rho_0^{-1}$ for the reaction $A+B\rightarrow 0$ on $d=2$ tubular lattices. The initial concentration is $\rho_0=0.4$. The width W is, from bottom to top, 2, 4, 8, 16, 32, and 64. $L=100\,000$ and the run is equal to 15.

$$t_c^{d/4}\sim W^{\beta}t_c^{1/4}, \tag{8}$$

which turns out to be $t_c\sim W^{\alpha}$, where

$$\alpha=\frac{4\beta}{d-1}. \tag{9}$$

For the reaction $A+B\rightarrow 0$ the exponent β cannot be obtained by the previous depletion zone argument because there is no reaction between same species particles. We measured the power exponent β from the simulation data, which turns out to be $\beta\sim 0.5$ for $d=2$ (Fig. 1) and $\beta\sim 1$ for $d=3$ (Fig. 2), respectively. Therefore, we predict a universal scaling result $t_c\sim W^2$ for large W. Furthermore, from Eq. (7) we can propose a scaling theory [10] of ρ_A for the reaction $A+B\rightarrow 0$:

$$\rho_A^{-1}\sim t^{d/4}f(t/W^{\alpha}), \tag{10}$$

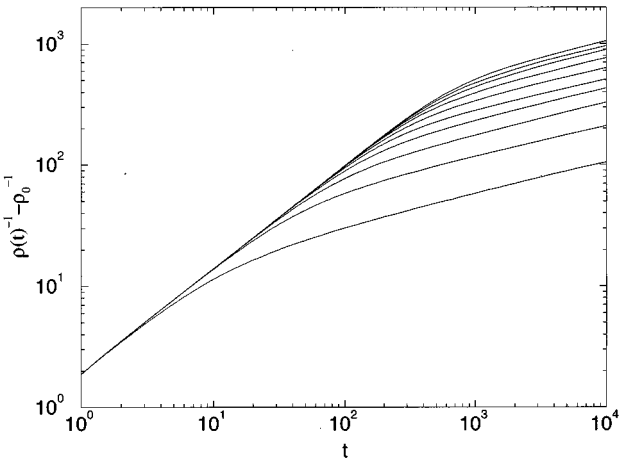

FIG. 2. Concentration $\rho(t)^{-1}-\rho_0^{-1}$ for the reaction $A+B\rightarrow 0$ on $d=3$ tubular lattices. The initial concentration is $\rho_0=0.4$. The width W is, from bottom to top, 3, 6, 9, 12, 15, 18, 21, 24, 27, and 30. $L=10\,000$ and the run is equal to 15.

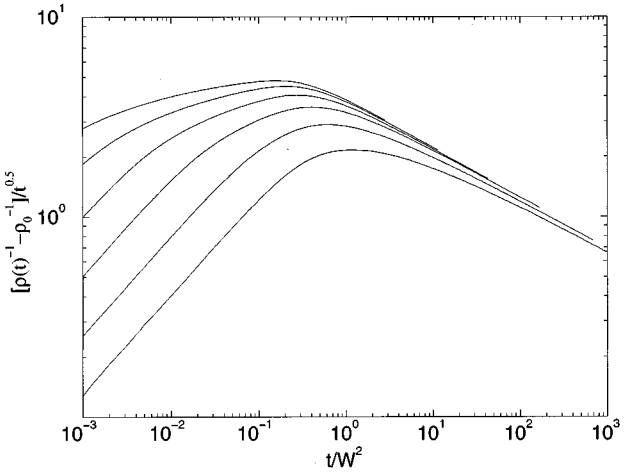

FIG. 3. Data collapse of concentration for the reaction $A+B\rightarrow 0$ on $d=2$ tubular lattices. The initial concentration is $\rho_0=0.4$. The width W is from 2 to 128. The parameters are described in the caption of Fig. 1.

where $f(x)\sim$const when x is small and $f(x)\sim x^{-\beta/\alpha}$ when x is large. Data collapse for $d=2$ (Fig. 3) and $d=3$ (Fig. 4) verifies the above scaling conjecture. The failure of data collapse at early times is due to the existence of the classic region at the very beginning of the reaction.

The behavior of t_c can be understood by studying the spatial correlation function of the concentration difference $\gamma(\vec{r},t)\equiv\frac{1}{2}[\rho_A(\vec{r},t)-\rho_B(\vec{r},t)]$. It can be easily shown that $\rho(\vec{r},t)$ obeys the diffusion equation [11]. Thus, for random initial conditions [12] the spatial correlation of ρ evolves as

$$\langle\gamma(\vec{r}_1,t)\gamma(\vec{r}_2,t)\rangle\sim\frac{1}{2(8\pi Dt)^{d/2}}e^{-(\vec{r}_1-\vec{r}_2)^2/4Dt}. \tag{11}$$

The above formula implies that the size of the self-segregation zone grows as $t^{1/2}$. We argue that the crossover time t_c on the tubular lattice happens when the self-segregation size reaches the width W.

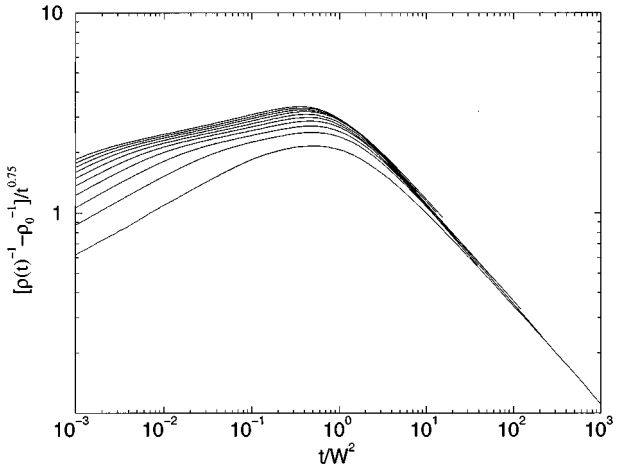

FIG. 4. Data collapse of concentration for the reaction $A+B\rightarrow 0$ on $d=3$ tubular lattices. The parameters are described in the caption of Fig. 2.

The discrepancy between our result and that in [7] comes from the different method employed to determine the crossover time t_c. In [7] the crossover time t_c is obtained for the $A+B\rightarrow 0$ process by drawing ''best'' linear fits to both the *early time* and the asymptotic time. However, for small W the early time decay of reactants weakly depends on W. This transient behavior is due to the finite size of the system: In Ref. [7] the survival probability ρ_c/ρ_0 vs W is plotted, where ρ_c is the density of A particles remaining on the lattice at the crossover time t_c. Compared with another survival probability ρ_0'/ρ_0, namely, the normalized densities at t_c', where t_c' is the crossover time to the Ovchinnikov-Zeldovich time regime in free space, it is found that, for $W\leqslant 10$, the finite-size effect sets in before one can observe the Ovchinnikov-Zeldovich behavior. This can also be confirmed by the data collapse: The flat portion of the scaling function $f(x)$ appears only when W is large enough.

Therefore, our scaling exponent is different from that in [7] because of the different definition of crossover time. In [7] the crossover time is actually the time at which the system enters the one-dimensional Ovchinnikov-Zeldovich behavior regime. For large W this definition approaches ours. However, the validity of scaling formula (7) in the long time regime still holds and actually can be used [13] to interpret the anomalous scaling exponent in [7] if the early (for small W) scaling behavior is carefully measured.

In three-dimensional free space it is difficult to observe the Ovchinnikov-Zeldovich decay $\rho^{-1}\sim t^{3/4}$ for reaction $A+B$. Recent study [14] shows that periodic boundary conditions act as effective convection currents, especially in three dimensions, and thus hinder the system's transition to the Ovchinnikov-Zeldovich regime. Using instead reflective boundary conditions improves this situation. However, in our method it can be seen that the measurement of the crossover time does not involve the high-dimensional Ovchinnikov-Zeldovich regime. We also tried the reflective boundary condition along the W direction and obtained a similar result.

V. CONCLUSIONS AND SUMMARY

In summary, we analytically solved the random-walk problem on tubular lattices and thus obtained an understanding of the scaling behavior of the crossover time for the reaction $A+A\rightarrow 0$. Applying data collapse technique we found, for large W, a normal scaling exponent of the crossover time for the reaction $A+B\rightarrow 0$ on tubular lattices. The discrepancy of our result with those of others is analyzed.

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APPENDIX A: HOW TO SOLVE S_n IN FREE SPACE

In this section we briefly review [8,15] the technique to obtain S_n, the number of distinct sites visited by a random walker in free space. Let us first define $p_n(\vec{j})$, the probability that the walker reaches site $\vec{j}$ at step n, and $f_n(\vec{j})$, the probability that the walker reaches site $\vec{j}$ at step n for *the first time*.

From the translational invariance property of the free space we have

$$p_n(\vec{j})=\delta_{n,0}\delta_{\vec{j},\vec{0}}+\sum_{k=1}^{n} f_k(\vec{j}\vec{j})p_{n-k}(\vec{0}). \tag{A1}$$

Furthermore, we introduce generating functions

$$p(\vec{j};z)=\sum_{n=0}^{\infty} p_n(\vec{j})z^n, \tag{A2}$$

$$f(\vec{j};z)=\sum_{n=0}^{\infty} f_n(\vec{j})z^n, \tag{A3}$$

with $f_0(\vec{j})=0$ implied, and it is easy to see that

$$f(\vec{j};z)=\frac{p(\vec{j};z)}{p(\vec{0};z)}-\frac{1}{p(\vec{0};z)}\delta_{\vec{j},\vec{0}}. \tag{A4}$$

The probability that the walker reaches a *new* site at step n, denoted as Δ_n, is

$$\Delta_n=\sum_{\vec{j}} f_n(\vec{j}) \tag{A5}$$

and therefore S_n, the number of distinct sites visited by the walker, can be expressed as

$$S_n=\sum_{k=1}^{n}\Delta_k.$$

The corresponding generating functions of Δ_n and S_n satisfy

$$\Delta(z)=\frac{z}{(1-z)p(\vec{0};z)}$$

and

$$S(z)=\frac{z}{(1-z)^2p(\vec{0};z)}. \tag{A6}$$

The asymptotic behavior of S_n can be related, via the Tauberian theorem [16], to the singularity of $S(z)$ at $z=1$.

APPENDIX B: HOW TO SOLVE S_n IN A TUBULAR GEOMETRY

Next we are going to prove formula (2) in this paper. Noticing that the d-dimensional tubular lattice is infinitely long in one (x) direction and of width W in the remaining directions ($\vec{y}$), we define $p_n(x,\vec{y})$ as the probability that the walker reaches site $(x,\vec{y})$ at step n. Here $\vec{y}$ is in $(d-1)$-dimensional subspace where periodic conditions with period W are implied. Since translational invariance still holds in this tubular geometry, we have

$$p_{n+1}(x,\vec{y})=\sum_{x',\{\vec{y'}\}} p(x-x',\vec{y}-\vec{y'})p_n(x',\vec{y}), \quad \text{(B1)}$$

where $p(x,\vec{y})$ is the single-step jump probability and x runs over all the integer numbers while $\{\vec{y'}\}$ runs over all the lattice sites in a $d-1$ cube of width W. A Fourier transform can be used to solve $p_n(x,\vec{y})$:

$$\hat{p}(\theta,\vec{s})\equiv\sum_{x,\{\vec{y}\}} p(x,\vec{y})e^{i(\theta x+2\pi\vec{s}\cdot\vec{y}/W)} \quad \text{(B2)}$$

or

$$p(x,\vec{y})\equiv\frac{1}{W^{d-1}}\sum_{x,\{\vec{y}\}}\frac{1}{2\pi}\int_{-\pi}^{\pi}\hat{p}(\theta,\vec{s})e^{-i(\theta x+2\pi\vec{s}\cdot\vec{y}/W)}. \quad \text{(B3)}$$

It can be easily shown that

$$\hat{p}_n(\theta,\vec{s})=[\hat{p}(\theta,\vec{s})]^n \quad \text{(B4)}$$

if the random walker is released from the origin. The $\hat{p}(\theta,\vec{s})$ for our tubular geometry is

$$\hat{p}(\theta,\vec{s})=\frac{1}{d}[\cos\theta+\cos(2\pi s_1/W)+\cdots+\cos(2\pi s_{d-1}/W)]. \quad \text{(B5)}$$

The relationship (A6) between $S(z)$ and $p(x,\vec{y};z)$ still holds for the tubular geometry and

$$p(0,\vec{0};z)=\frac{1}{W^{d-1}}\sum_{\{\vec{s}\}}\int_{-\pi}^{\pi}\frac{1}{1-z\hat{p}(\theta,\vec{s})}\frac{d\theta}{2\pi}.$$

Singularity happens only when $s_1=s_2=\cdots=s_{d-1}=0$. Therefore,

$$p(0,\vec{0};z\to 0)=\frac{1}{W^{d-1}}\int_{-\pi}^{\pi}\frac{1}{1-z(\cos\theta+d-1)/d}\frac{d\theta}{2\pi} \quad \text{(B6)}$$

$$\sim\frac{1}{W^{d-1}}\int_{-\infty}^{\infty}\frac{1}{(1-z+z\theta^2/2d)}\frac{d\theta}{2\pi} \quad \text{(B7)}$$

$$=\frac{\sqrt{d}}{W^{d-1}}\int_{-\infty}^{\infty}\frac{1}{(1-z+z\theta^2/2)}\frac{d\theta}{2\pi}. \quad \text{(B8)}$$

The integrand in the identity (B8) can be recognized as that of the random walk in one-dimensional free space and thus we get

$$S_n\sim\frac{W^{d-1}}{\sqrt{d}}\sqrt{\frac{8n}{\pi}}. \quad \text{(B9)}$$

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