Simulation of the Wiener sausage

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The volume of a region visited by a spherical Brownian particle for a time t, known as the Wiener sausage, is an important random variable characterizing Brownian motion. A Brownian dynamics simulation is used to study statistical properties of the Wiener sausage volume. We show that the probability density is closely approximated by a Gaussian distribution not only at asymptotically long times, but over a wide range of times as well. We also refine the expression for the dispersion by finding a correction term for the long-time asymptotic dependence.

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The spatial region visited by a spherical Brownian particle for a time t is known as the Wiener sausage (WS) (see Fig. 1), from Kac [1]. Leontovich and Kolmogorov [2] were the first to demonstrate that the volume of the WS is an important random variable characterizing Brownian motion. Attempts at determining statistical properties of the WS volume (as well as the cognate problem of the number of distinct lattice sites visited by a random walker [3–8]) are motivated both by many interesting mathematical issues [9,10] and the number of physical, chemical, and biological applications [11,12] that call for a knowledge of this random variable. One source of the particular interest in this class of problems is that of improving the initial Smoluchowski theory of diffusion-controlled reactions [12].

Analytical approaches and numerical simulations are complementary in their consideration of the problem under study. Due to analytical treatments [1,2,10,13–16] considerable progress has been made in understanding the statistical properties of the WS volume, mainly at long times. At intermediate and short times the problem is less well understood. The formulas obtained are not asymptotic series and there is no indication of how large t has to be to ensure that the given formulas become valid. In particular, it is known (due to Le Gall [13]) that, in high dimensions ($d \geqslant 3$) the limiting ($t \to \infty$) distribution is Gaussian; however, no information is available on when this limit is reached. The most efficient method for solving problems of such type is a Brownian dynamics simulation. Brownian dynamics is an off-grid method for simulating diffusion processes, which is not restricted to a finite simulation box [17,18]. It is based on the isomorphism between the diffusion and Langevin equations. As far as we are aware, the Brownian simulation has never been applied to analysis of the WS.

With this in mind, we have simulated stochastic trajectories of a spherical Brownian particle, counted directly the volume visited by the particle, and calculated the average value, the dispersion, and the probability density of the WS volume. The results obtained in the three-dimensional case are presented in this paper. First, to verify our method of simulation we compare the computed result for the average volume with the known analytical solution [16] and find very good agreement between them. Then, we show that the limiting expression for the dispersion [16] becomes a useful approximation at very long times only and find a correction term that allows a refined calculation of the dispersion at intermediate times (note that an analytical calculation of the correction term is a hard mathematical problem). To the contrary, the Gaussian distribution fits the probability density (save its long tails) surprisingly well, not only at asymptotically long times, but over a wide range of times as well.

As a concluding remark, we shall discuss the relationship between the WS volume characterizing continuous diffusion and the range of a random walk (the number R_n of distinct sites visited by an n-step lattice random walk) used in considering the analogous discrete process. The theory of the range of a random walk was initiated by Dvoretzky and Erdös [3] and developed in subsequent articles [4–7] (see Ref. [8] for a general review). The similarity of a Brownian motion trajectory and a random walk is well known [19]. Perhaps this could have been the motivation for the seemingly widespread opinion that R_n is simply a discrete analog of the WS volume, and the difference between these quantities is not significant. We show that this opinion is generally not valid because the similarity of trajectories does not imply the similarity of functionals of trajectories. Only in low-dimensional spaces ($d=1,2$) are the WS volume and the range of a random walk proportional to one another.

We begin by recalling some relevant definitions and

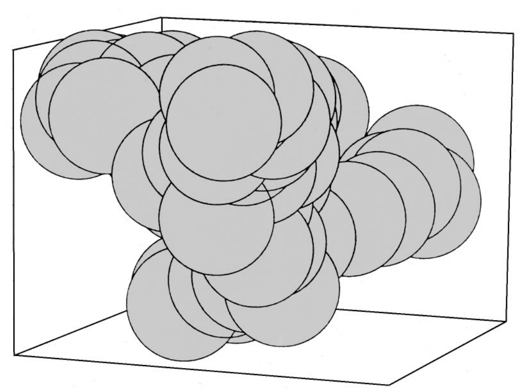

FIG. 1. A sample of a typical Wiener sausage generated by Brownian dynamics simulation.

known analytical results to be used in the subsequent analysis. Consider a spherical Brownian particle of radius b. By introducing an indicator function

$$I_b(\mathbf{r},W_t)=\begin{cases}1 & \text{if } \min|\mathbf{r}-\mathbf{r}_{W_t}|\leq b\\ 0 & \text{otherwise}\end{cases}\tag{1}$$

where $\mathbf{r}_{W_t}\in W_t$, the volume of WS that corresponds to a given Wiener trajectory W_t of the particle center can be formally defined as

$$v(W_t)=\int I_b(\mathbf{r},W_t)d\mathbf{r}.\tag{2}$$

The random variable $v(W_t)$ is distributed with the probability density $F_t(v)\equiv\langle\delta[v-v(W_t)]\rangle$ (the symbol $\langle\cdots\rangle$ stands for the average over the Wiener trajectories). Analytical calculation of the probability density $F_t(v)$ characterizing the distribution of the WS volume v at time t is a hard mathematical problem. An exact solution has been found only in one dimension for both free [15,16] and biased Brownian motion [20]. In high dimensions $(d\geq 3)$, the probability density near its maximum takes on the Gaussian form when $t\to\infty$ [13],

$$F_t(v)=\frac{1}{\sqrt{2\pi}\sigma(t)}\exp\left(-\frac{[v-\overline{v}(t)]^2}{2\sigma^2(t)}\right),\tag{3}$$

where $\overline{v}(t)\equiv\langle v(W_t)\rangle$ is the average of the WS volume and $\sigma^2(t)$ is the dispersion. In accordance with the definitions Eqs. (1) and (2), the average of $v(W_t)$ is expressed via the average of the indicator function. The quantity $\langle I_b(\mathbf{r},W_t)\rangle$ is equal to the probability that a diffusing particle is absorbed by the only trap of radius b for time t, initially at distance r, which is a well known solution of the isolated pair problem. Using this fact, one has [16]

$$\overline{v}(\tau)=3v_0(\tau+2\sqrt{\tau/\pi}+\tfrac{1}{3}),\tag{4}$$

where $\tau=Dt/b^2$ is the dimensionless time, D is the diffusion coefficient, and $v_0=\frac{4}{3}\pi b^3$ is the volume of the Brownian particle.

To find the dispersion $\sigma^2(t)$ one has to focus on the average of the square of the WS volume, $\overline{v^2}(t)\equiv\langle v^2(W_t)\rangle$, because

$$\sigma^2(t)=\overline{v^2}(t)-\overline{v}^2(t).\tag{5}$$

From the definition of the WS volume [see Eqs. (1) and (2)], it follows that the second moment $\overline{v^2}(t)$ can be expressed through the absorbing probability of a Brownian particle in the presence of one and two traps. In the two-trap situation it is difficult to calculate the absorbing probability for arbitrary position of the traps. A simple approximate method to treat the problem at long times was proposed in Ref. [16], where, as a result, three main terms of the long-time expansion of $\overline{v^2}(t)$ were found. The first two coincide with the two main terms of the long-time expansion of $\overline{v}^2(t)$. Thus, the result obtained in Ref. [16] can be written in the form

$$\sigma^2(\tau)=9v_0^2[\tau\ln\tau-A\tau+o(\tau)]\quad\text{for }\tau\gg 1.\tag{6}$$

The approximation used in Ref. [16] is too crude for calculating the coefficient A determining the correction term for the long-time expansion of the dispersion. However, without the correction term one cannot decide where the asymptotic behavior $\tau\ln\tau$ predicted by the main term becomes valid and Eq. (6) is meaningful only in the limit $\tau\to\infty$. One of our motivations to carry out statistical simulation of the WS is to estimate the coefficient A and, hence, to elucidate the long-time behavior of the dispersion. Another motivation is to look at how the Gaussian distribution fits the probability density $F_t(v)$ at different times.

To simulate the WS first it is necessary to simulate stochastic trajectories of the center of a freely diffusing spherical particle. The trajectories are generated from a series of successive Brownian steps by employing the original step algorithm of Ermak and MacCammon [17]. In a given run, the particle center moves through a sequence of points $\{\mathbf{r}_i\}$, $i=1,2,\ldots$. The ith hop occurs during a predefined time interval Δt, so that the trajectory is propagated according to

$$\mathbf{r}_{i+1}=\mathbf{r}_i+\sqrt{2\Delta t}\mathbf{g},\tag{7}$$

where the vector $\mathbf{g}$ is generated stochastically as a set of Gaussian random numbers with a standard deviation of unity (the diffusion coefficient is set to unity). In order to compute the volume of the WS corresponding to a given trajectory, we embed the trajectory into a cubic box. This box is partitioned into small cubic boxes of size $\alpha<1$ (the particle radius b is set to unity). Following the definition of the WS volume, Eqs. (1) and (2), we consider a small box as "visited" if the minimal distance of its center from the trajectory is less than 1. Then we count the number of "visited" small cubes and find the WS volume. The results are averaged over 1000 trajectories. We performed additional analysis and found that $\Delta t=0.01$ (with this set of units $t=\tau$) and $\alpha=0.25$ are optimal values for Δt and α from the viewpoint of accuracy of the calculation and time and memory consumption. Note also that for a spherical Brownian particle our method of gauging the volume leads to an overestimate of v. To refine the estimate, the result of calculation of the WS volume is rescaled by a factor of 0.96 (this value of the correction factor was chosen because it allows us to reach a perfect agreement between the average volume of the WS found by simulations and the analytical result, which is exact).

A sample of a typical WS generated according to the above method is shown in Fig. 1. It demonstrates well the entangled behavior of particle trajectories and the complicated structure of the WS. In Fig. 2 we present the Brownian dynamics simulated results for the average volume of the WS at different times in comparison with the exact time dependence $\overline{v}(\tau)$ given by Eq. (4). Such a comparison serves as a test of accuracy of our simulation. Even at short times $\tau<10$, where the accuracy of measuring the volume is relatively low, deviations do not exceed 3%, while at longer times $\tau>100$, they are less than 0.5%. The fact that the computed and analytical results for the average volume are in very good agreement allows us to apply the method to the study of more detailed properties of the WS volume distribution.

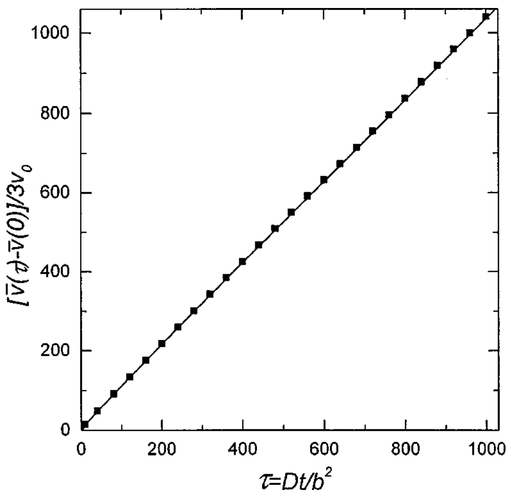

FIG. 2. Comparison of the analytical solution for the average WS volume [Eq. (4)] (solid line) with simulation data (squares).

Figure 3 presents the results of calculations of the dispersion $\sigma^2(t)$. As one might expect, only the main term of the asymptotic dependence [see Eq. (6)] makes too crude an estimate of the dispersion not only at short times but also at intermediate times ($\tau \sim 10^3$). Taking properly into account the linear correction term brings the theory and the computer experiment into better agreement. The statistical processing of simulated data (at the times $900 \leqslant \tau \leqslant 1000$ best suited for our goals) suggests that the coefficient A is equal to 4.42 ± 0.02 (the surprising thing is that the crude estimate $A \approx 4.71$, derived by the method [16] whose accuracy is too low for the correct calculation of A, is probably not much in error). Thus only at times $\tau > 10^{20}$ does the main term in Eq. (6) by itself give a more or less adequate (with accuracy 10%) estimate of $\sigma^2(t)$. With $A = 4.42$, Eq. (6) allows a refined calculation of the dispersion at $\tau > 500$.

All of the relevant properties of the WS volume can be expressed in terms of the probability density $F_t(v)$. When considered as a function of v, $F_t(v)$ has a bell-shaped form. In the course of time the peak shifts to infinity and its width

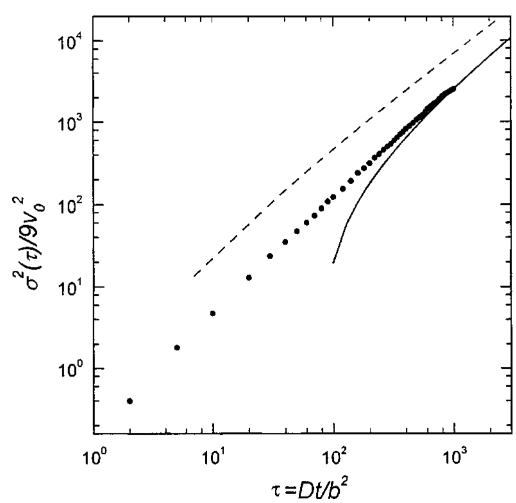

FIG. 3. Comparison of the analytical solution for the dispersion [Eq. (6)] with $A = 4.42$ (solid line) with simulation data (circles). Dashed line corresponds to the long-time asymptotic behavior given by only the main term of Eq. (6).

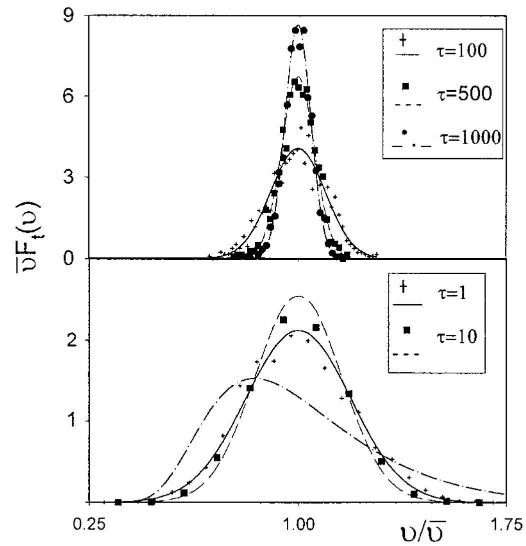

FIG. 4. Time evolution of the probability density of the WS volume. Different panels correspond to different ranges of time. The results of the simulations (averaged over 10 000 and 1000 trajectories for the bottom and top panels, respectively) are presented by symbols. The curves correspond to the Gaussian distribution, Eq. (2), with the parameters $\overline{v}(t)$ and $\sigma^2(t)$ calculated from simulation data. The legend gives the pattern correspondence. The dash-dotted line in the bottom panel represents the exact solution for the probability density of the WS volume in one dimension [15,16].

increases. The time evolution of the probability density is strikingly illustrated by Fig. 4, in which the volume v is scaled by $\overline{v}(\tau)$. In this figure we present the distribution of the WS volume at different times, obtained from simulation data. We also present the curves corresponding to the Gaussian distribution, Eq. (2), with the parameters $\overline{v}(\tau)$ and $\sigma^2(\tau)$ found from the results of simulation. For comparison (in the bottom panel) we add the probability density of the span of Brownian motion (the one-dimensional analog of the WS volume), which can be calculated exactly [15,16]. Note that this curve exhibits a non-Gaussian distribution of the span and is independent of time.

As indicated in Fig. 4 (bottom panel), even at short times ($\tau \lesssim 10$) the Gaussian distribution is a satisfactory approximation for the probability density. This is in contrast with what is known for the one-dimensional case. The non-Gaussian behavior in one dimension is due to the memory among the increments of the ''volume'' visited by a Brownian particle at different instances of time. Because in three dimensions the Brownian motion is a transient process (in the one-dimensional case the process is recurrent), the memory effects are weakened in the course of time. The important consequences of this fact are the linear dependence of the average volume on time and the Gaussian form of the probability density at $\tau > 1$. We would like to stress, however, that these effects do not disappear even at asymptotically long times. Just the memory effects are responsible for the non-Gaussian behavior in the far tails. Moreover, the nonlinear long-time asymptotic behavior of the dispersion is also a manifestation of non-Markovian properties of the WS volume.

As Fig. 4 suggests, with time the normalized bandwidth associated with the relative fluctuation $\tilde{\sigma}(\tau) = \sigma(\tau)/\overline{v}(\tau)$

rapidly decays. At times $\tau > 100$ (top panel), the Gaussian distribution becomes a very good approximation for the probability density. This is in agreement with the central limit theorem for $F_t(v)$ proved by Le Gall [13]. Moreover, our results show that in fact the probability density $F_t(v)$ takes on the Gaussian form not only at asymptotically long times but at intermediate times as well. Of course, such a conclusion holds true only for volumes that are not too far from $\overline{v}(\tau)$ (our estimates show that the halfwidth of this interval is at least of order 10σ at times $\tau = 1000$). As shown by Donsker and Varadhan [14], the small-v behavior of $F_t(v)$ obeys an $\exp(-\text{const}\times Dt/v^{2/3})$ law. Unfortunately, the accuracy of our simulation is too low to handle the large deviations and non-Gaussian behavior in the far tails.

Our last remark is that the WS volume is similar but not identical to the number of distinct sites visited by a random walk (the range of the random walk) characterizing the analogous discrete process. In order to demonstrate this, let us compare the trajectory of the Brownian particle center to an n-step ($n \gg 1$) random walk on a simple cubic lattice with period l. For time t such a walk executes

$$n = 6Dt/l^2 = 6(b/l)^2\tau \tag{8}$$

steps and visits R_n distinct lattice sites. Note that a continuous description implies that the particle radius b appreciably exceeds its mean free path, whose role is played by the lattice period l, i.e., $b \gg l$ (the lattice consideration is justified in the opposite limiting case, $l \gg b$). For large n, the distribution of R_n is Gaussian [5] and can be specified by the average value $\overline{R_n}$ and the dispersion σ_n^2 of the range, which are asymptotically [4–6]

$$\begin{aligned} \overline{R_n} &\simeq 0.718[n + 0.729\sqrt{n} + O(1)], \\ \sigma_n^2 &= 0.215[n \ln n - Bn + o(n)] \end{aligned} \tag{9}$$

(the coefficient B was found numerically to be $B \approx 4.17$ [7]). Let us compare the relative fluctuation of the WS volume, $\tilde{\sigma}(\tau)$, with that of the range, $\tilde{\sigma}_n = \sigma_n/\overline{R_n}$. In one and two dimensions, the ratio $\tilde{\sigma}(\tau)/\tilde{\sigma}_n$ is equal to unity (one can check this using the results obtained in Refs. [4–6], [16]), i.e., the quantities discussed are identical. In three dimensions, however, this is not the case. Indeed, according to Eqs. (4), (6), (8), and (9), we have asymptotically

$$\hat{\sigma}(\tau)/\tilde{\sigma}_n \simeq 3.79b/l, \tag{10}$$

i.e., v and R_n are not proportional to one another. The point is that the discrete analog of the WS volume is the number $R(n;b)$ of distinct sites visited by a sphere of radius $b \gg l$, the center of which executes random walks on the lattice. Evidently, for $d > 2$, where the Brownian motion is a transient process, the statistical properties of $R(n;b)$ differ from those of R_n. The distinction occurs at any $b > l$. Thus, only in low-dimensional spaces, where the process is recurrent, are the WS volume and the range of the random walk proportional to one another.

To summarize, we have performed a quantitatively accurate Brownian dynamics numerical simulation of the WS. We have studied the statistical properties of the volume of the WS. Our main result is that the Gaussian distribution fits the probability density surprisingly well, not only at asymptotically long times, but over a wide range of times as well. We have also demonstrated that the limiting expression for the dispersion is a useful approximation at very long times only, and found a correction term that allows a refined calculation of the dispersion at intermediate times. Along with the general theory of random processes the results of the present paper may be useful when considering diffusive processes in which the particle size far exceeds its mean free path. The results obtained in the two-dimensional case will be reported elsewhere.

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