Efficient modified ''walk on spheres'' algorithm for the linearized Poisson–Boltzmann equation

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(Received 27 October 2000; accepted for publication 12 December 2000)

A discrete random walk method on grids was proposed and used to solve the linearized Poisson–Boltzmann equation (LPBE) [R. Ettelaie, J. Chem. Phys. **103**, 3657 (1995)]. Here, we present an efficient grid-free random walk method. Based on a modified ''walk on spheres'' algorithm [B. S. Elepov and G. A. Mihailov, Sov. Math. Dokl. **14**, 1276 (1973)] for the LPBE, this Monte Carlo algorithm uses a survival probability distribution function for the random walker in a continuous and free diffusion region. This simulation method is illustrated by computing four analytically solvable problems. In all cases, excellent agreement is observed. © *2001 American Institute of Physics.* [DOI: 10.1063/1.1345817]

Random walk methods have been used to solve a wide variety of parabolic and elliptic partial differential equations (PDEs).[1–5] Generally, there are two broad classes of random walk methods; one uses discrete random walks on grids,[1] and the other continuous random walks in free space.[2–5] One of the widely used continuous random walk methods, the ''walk on spheres'' (WOS) method,[2,6–8] uses the first-passage probability distribution on a sphere to facilitate large steps in random walks. (The first-passage probability, $w(x;x_0)$, is the probability of hitting the vicinity of x on the bounding surface when the random walker starts from x_0, a point inside the bounding surface.) This continuous random walk method needs to discretize neither space nor time, nor the diffusing trajectory, and so it is particularly advantageous when the geometry of the region of interest is very complex or if the solution of the PDE is required at only a relatively small number of points.

We are interested in solutions to the Dirichlet problem for the linearized Poisson–Boltzmann equation (LPBE) in the domain Ω:

$$\nabla^2\psi(x)=\kappa^2\psi(x), \quad x\in\Omega, \tag{1}$$

$$\psi(x)=\psi_0(x), \quad x\in\partial\Omega, \tag{2}$$

where κ is called the inverse Debye length.[1] Notice that when κ^2 is zero, the earlier problem becomes a Dirichlet problem for the Laplace equation. The WOS method for the Dirichlet problem for the Laplace equation has been widely used.[2,6,7,3,9,10] We will combine this WOS method with a survival probability density function which incorporates the term involving κ^2 in the LPBE.

In a discrete random walk method[1] for the LPBE, the corresponding Master equation relates κ^2 to the removal probability of the random walker on the grid. During each step of the discrete random walk, the walker either moves to one of the neighboring sites, or stays fixed, or is removed. This probabilistic interpretation of κ^2 can be also extended to continuous random walk methods once we know the survival probability distribution function of a random walker in continuous space.

In this letter, we obtain this survival probability distribution function of a random walker in continuous space by reinterpreting the weighting function in the previous modified WOS method[11] for the LPBE (see the Appendix for more details). The survival probability of a random walker in a continuous and free diffusion region is given by[11]

$$p(d)=d\kappa/\sinh(d\kappa), \tag{3}$$

where d is the distance from the starting point in the diffusion region. Figure 1 shows this probability density function. We modify the WOS method to incorporate the survival probability to solve the LPBE via a continuous random walk method. This probability density combined with the WOS method is used to remove a random walker during the random walk by the acceptance-rejection method.[12] We generate a random number, η in (0,1) when we perform a WOS

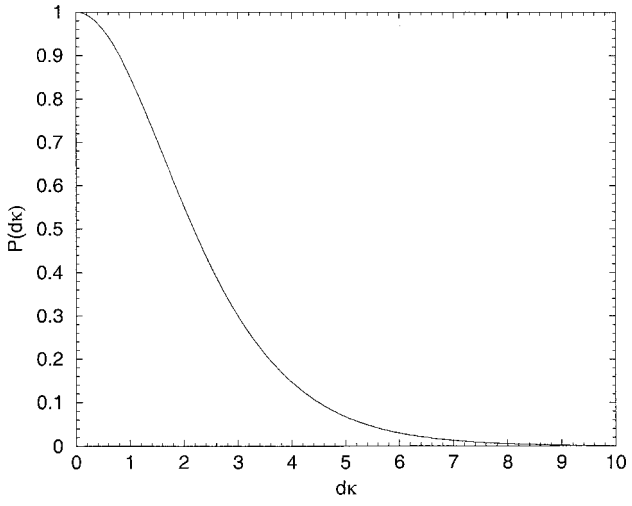

FIG. 1. The survival probability density function; d is the diffused distance of a random walker from the starting position, and κ is the inverse Debye length.

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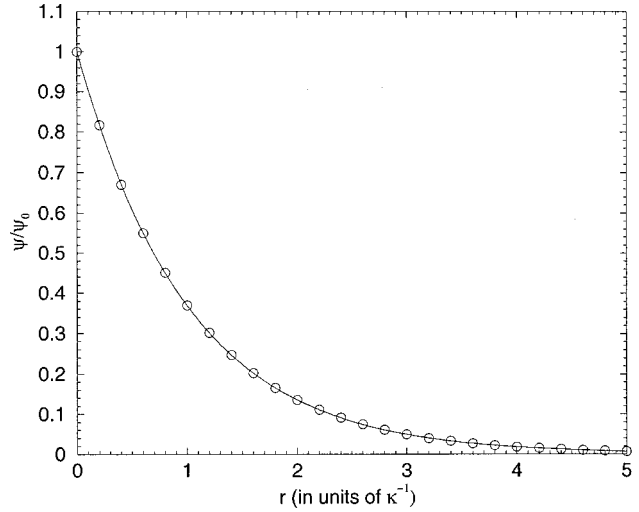

FIG. 2. The electric potential away from an charged infinite flat plate in an electrolyte; the solid line is the analytic solution and the circles are the simulation results with 10^5 random walks and the absorption layer $\delta = 10^{-4}$. Here, r is the distance to the plate and κ is the inverse Debye length.

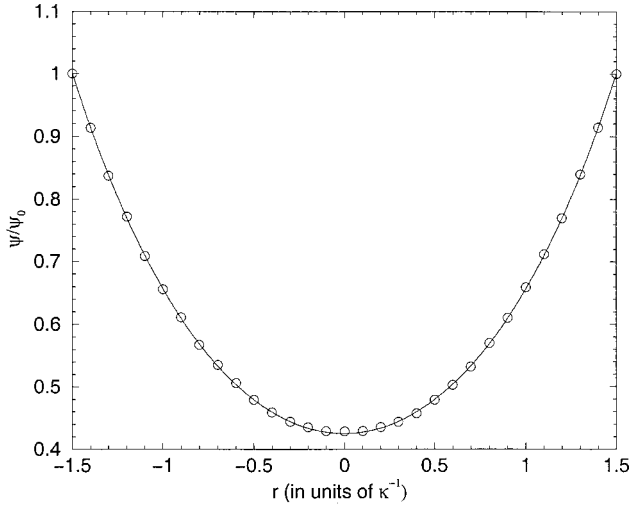

FIG. 3. The electric potential in an electrolyte between two infinite charged parallel flat plates; the solid line is the analytic solution and the circles are the simulation results with 10^5 random walks and the absorption layer $\delta = 10^{-4}$. Here, r is the distance from the mid-point of the plates and κ is the inverse Debye length.

step, and we compare η with $p(d)$, the survival probability at d, the radius of WOS. If $\eta > p(d)$, the random walker is removed at this WOS step.

An estimate for the solution of the LPBE at x_0, where random walkers start, is given by S_N:

$$S_N = \frac{1}{N} \sum_{i=1}^{N_s} \psi_0(X_{n_i}). \tag{4}$$

Here, N is the total number of random walkers, N_s is the number of survived-and-absorbed random walkers, and X_{n_i} is the final position of the walker on the boundary when it is absorbed after n_i WOS steps.

In this method, like the WOS method, errors are due to both statistical sampling and the δ-absorption layer which captures random walkers near the boundary to terminate their random walk. However, the error from the δ-absorption layer can always be made smaller than the statistical error.[6,7] For the same random walk, the estimate difference between using δ and $\delta/10$ gives a measure of the error due to the finite width of the δ-absorption layer. By adjusting δ we can make the error from the absorption layer less than the statistical error. This means that if we increase the number of random walkers to decrease the statistical error, consequently we must reduce δ and so increase the running time.

In the following, we compare our simulation results with the analytic results for four problems, which were used as examples for the discrete random walk method.[1] In all cases, the results are given as those normalized by the boundary condition ψ_0, which is assumed sufficiently small for the LPBE to be valid. The number of random walks used for the solution at a point is 10^5, and the absorption layer thickness is $\delta = 10^{-4}$. The analytic results[1] are shown with solid lines in Figs. 2–5 and our simulation results with circles. For the all four cases, our simulation results show excellent agreement. Our method has several features. First, it is easier to implement and will be faster than the other discretized methods, such as the discrete random walk method,[1] the finite difference method,[13] and the boundary-element method,[14] especially with complicated geometries. For a desired point, it takes only a few seconds to compute a solution with 10^5 random walkers and $\delta = 10^{-4}$ on a 550 MHz PC. However, it is hard to compare to other methods because they compute solutions at all grid points. We can safely say that continuous Monte Carlo methods are more efficient when the solution is required only at relatively small number of points. Second, the accuracy and the running time of our method depends primarily on the number of statistical samples, and so it is naturally parallel. Third, it is certain that our method is faster than the old modified WOS method,[11] because while some of our random walkers are removed during their random walk, in the old method all random walkers must complete their random walks to contribute to the solution according to their weightings. Also, in open boundary cases, like the three examples except the parallel plates, it is necessary to use a certain cutoff in the old modified WOS[11] to kill random

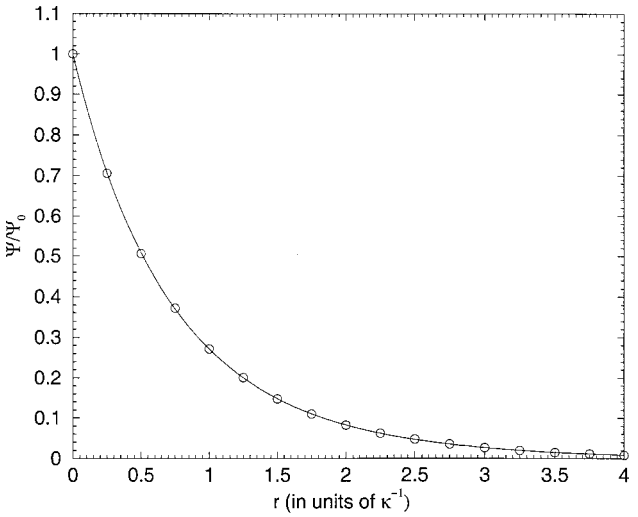

FIG. 4. The electric potential away from an infinitely long charged cylinder in an electrolyte; the solid line is the analytic solution and the circles are the simulation results with 10^5 random walks and the absorption layer $\delta = 10^{-4}$. Here, r is the distance from the surface of the cylinder with unit radius and κ is the inverse Debye length.

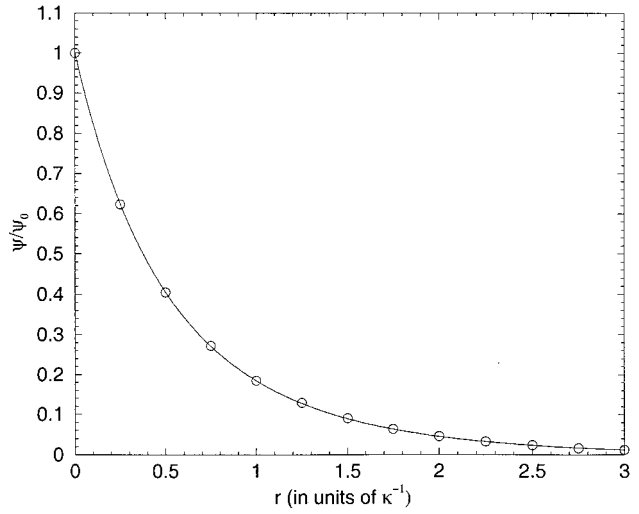

FIG. 5. The electric potential away from the surface of a charged sphere in an electrolyte; the solid line is the analytic solution and the circles are the simulation results with 10^5 random walks and the absorption layer $\delta = 10^{-4}$. Here, r is the distance from the surface of the sphere with unit radius and κ is the inverse Debye length.

walkers, which will bias the results. As an example, in Table I in the case of the parallel plates, we compare our method with the old modified WOS method.[11] We use the customary comparison method for Monte Carlo methods, the time consumption (or laboriousness):[15] $t\underline{D}\xi$, where t is the CPU time expended in calculating a single estimate and $\underline{D}\xi$ is the variance of the estimates. The less laborious the algorithm, the more efficient it is. In Table I, the time consumption (or laboriousness) of our algorithm is better than that of the old modified WOS method. Finally, our method is easy to extend to solve the LPBE with source terms.[11] That will be the subject of our upcoming research with biochemical applications.

TABLE I. Time consumption comparison of our algorithm with the old modified WOS in the case of parallel plates at the midpoint; the variances are obtained from 100 independent runs, the number of random walks per run is 10^5 and the absorption layer, $\delta = 10^{-4}$.

Method	CPU time per run (s)	Variance (10^{-7})	Time consumption (10^{-6})
Old method	13.47	4.63	6.24
Our method	2.97	19.8	5.88

In this appendix, we show how the weighting function in the old modified WOS method[11] can be interpreted as the survival probability distribution function. For simplicity, consider the LPBE in the old modified WOS method.[11] The solution at x_0 in the domain can be expressed as follows:[11]

$$u(x_0) = \frac{1}{N}\sum_{i=1}^{N} Q_i^{n_i}\psi_0(X_{n_i}), \tag{A1}$$

where

$$Q_i^0 = 1, \quad Q_i^{n_i} = Q_i^{n_i-1}\frac{d_i^{n_i-1}\kappa}{\sinh(d_i^{n_i-1}\kappa)}, \quad d_i^{n_i} = d(P_i^{n_i}). \tag{A2}$$

Here, N is the total number of diffusing random walkers, i refers to ith random walker, X_{n_i} is the position where the ith random walker is absorbed in the δ-absorption layer after n_i WOS steps, and $d_i^{n_i}$ the radius of n_ith WOS of the ith random walker.

If we interpret $Q_i^{n_i}$ as a survival probability of ith random walker, $\Sigma_{i=1}^{N} Q_i^{n_i}$ is the total number of survived-and-absorbed random walkers. Furthermore, due to the property of probabilistic random sampling from the total random walkers, only the survived-and-absorbed random walkers can be regarded as contributors to the solution. This reinterpretation of the weighting function as the survival probability distribution function is a kind of the fractional sampling method, i.e., ''Russian Roullete,''[12] which has been used extensively in neutron transport and similar problems.

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