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THE STATIONARY ARRIVAL PROCESS OF INDEPENDENT DIFFUSERS FROM A CONTINUUM TO AN ABSORBING BOUNDARY IS POISSONIAN*

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Abstract. We consider the arrival process of infinitely many identical independent diffusion processes from an infinite bath to an absorbing boundary. Previous results on this problem were confined to independent Brownian particles arriving at an absorbing sphere. The present paper extends these results to general diffusion processes, without any symmetries and without resorting to explicit expressions for solutions to the relevant equations. It is shown that for general absorbing boundaries and force fields, the steady stream of arrivals is Poissonian with rate equal to the total flux on the absorbing boundary, as calculated from the continuum theory of diffusion with transport. The considered arrival problem arises in the theory of Langevin simulations of ions in electrolytic solutions. In a Langevin simulation ions enter and exit the simulation region, and it is necessary to compute the probability laws for their entrance times into the simulation. While the simulated ions inside the small simulation region interact with each other and with the far field of the surrounding bath and the applied voltage, the physical chemistry continuum description of the surrounding bath implies independent diffusion in a mean field. Under these conditions the result of this paper applies to the stream of new ions that arrive from the continuum bath into the discrete simulation region. The recirculation problem, of ions that have already visited and exited the simulation region, as well as the integration of these results into a simulation of interacting ions will be studied in separate papers.

Key words. stochastic processes, diffusion, stochastic differential equations

AMS subject classifications. 60G35, 60J60, 60H10

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1. Introduction.

The study of the arrival process of diffusing particles from a continuum to an absorbing boundary started at the earliest stages of the probabilistic theory of diffusion. In 1917, Smoluchowski [1] (see also [2], [3]) calculated the flux on an absorbing sphere immersed in an infinite bath of independent Brownian particles with fixed concentration at infinity and applied his result to the theory of coagulation of colloids. The time to the arrival of the first Brownian particle from an equilibrated continuum bath to an absorbing sphere was shown by Bordewijk in 1975 [4] to be exponentially distributed with rate equal to the Smoluchowski flux. That result was applied to the theory of defect relaxation in dielectrics. Obviously, the existence of a stationary flux, which represents the average number of absorbed particles per unit time, does not imply in general that the first arrival time or any other interarrival times are exponentially distributed. The flux and the exponential rate coincide only for Poisson processes [5], [6]. The proof that all interarrival times of free Brownian particles at the absorbing sphere are identically exponentially distributed, thus rendering the absorption process Poissonian with rate equal to the Smoluchowski flux, was given by Nadler in 1994 [7]. All of these results concern problems with spherical symmetry and rely on explicit known solutions of the relevant equations.

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The probabilistic characterization of the arrival process of particles into an absorbing boundary also has important applications, apart from its mathematical interest and history. This problem arises, for example, in the simulation of discrete particles in a finite region of a continuum bath. A common approach in these simulations is to define a relatively small finite simulation region, start with an initial configuration of the required (average) number of particles inside the simulation region, and move the particles according to their dynamics. The two most common treatments of the boundaries of the simulation region are to define them as reflecting or periodic boundaries [8]. In both treatments of the boundaries, the total number of particles inside the simulation region is fixed at all times. Thus, all fluctuations in the number of particles inside the simulation region are lost, and all physical phenomena related to these fluctuations may not be recovered correctly by the simulation. Of course, if the simulation region is large enough, then in a small subregion of the simulation fluctuations in the number of particles do exist, but then the simulation itself might be infeasible in terms of computer resources due to the large number of simulated particles in the larger region. A different approach, as described in [7], [9], is to simulate the motion of particles in only a small region, but also on the one hand to let the particles exit the simulation region and be absorbed by the continuum bath, and on the other hand let particles from the continuum bath enter the simulation region. In such a simulation scheme, the total number of particles inside the simulation region is not fixed, but rather fluctuates in time. The exact absorption and injection mechanisms between the continuum bath and the discrete simulation region should of course mimic as much as possible the situation in the real physical system and maintain the correct average number of particles in the simulation region. To carry out such a simulation it is necessary to compute the statistics of these mechanisms, in particular the arrival times of particles from the continuum bath into the simulation region. Arrivals of particles into the simulation region can be divided into two types: (i) arrivals of "new" particles, which have not visited the simulation region so far and (ii) arrivals of "returning" particles, which have already visited and exited the simulation region. In this paper we study arrival process (i). The more complicated process (ii) will be studied in a separate paper. The integration of processes (i) and (ii) into a simulation of interacting ions in solution will be done in still another paper.

In this paper, we generalize the results obtained so far to general diffusion processes and general boundaries without any symmetries and without explicit solutions to the relevant equations. We consider an infinite three-dimensional bath of independent noninteracting Brownian particles diffusing in the presence of a general force field and an absorbing boundary with general geometry. The main result of this paper is that the steady state absorption stream at an absorbing boundary of particles diffusing independently in a force field is Poissonian with rate equal to the total absorption flux. The significance of this result for simulations of ions in solution is that the arrival process of new particles into the simulation is *memoryless* when the assumptions of independent diffusion are satisfied outside the simulation region. This means that the interarrival times of new particles into the simulation region are independent identically distributed (i.i.d.) random variables and can be easily generated without the need to store the history of previous arrival times.

It is a common practice in physical chemistry to describe ionic solutions by an electrochemical potential. This means that the motions of ions in solution are assumed to be independent diffusion processes in a mean force field. To compensate for the lost interionic interactions an *activity factor* is introduced [10]. Thus, our assumptions are satisfied in regions that can be described by independent diffusion (usually outside

the simulation region).

The paper is organized as follows. In section 2 the flux in a one-dimensional problem is computed, and in section 3 we show that the first arrival time is exponentially distributed with a rate that equals the calculated flux. The first arrival time in a general three-dimensional setting is formulated and solved in section 4. The probability law of all subsequent interarrival times is calculated in section 5. Finally, a summary and discussion are given in section 6.

2. The stationary flux at an absorbing boundary in one dimension. We begin with a simplified one-dimensional model of a continuum bath and an absorbing boundary. In this section we calculate the continuum *flux* into the absorbing boundary, and in the next section we show that the *distribution* of the first arrival time at the same boundary is exponential with a rate that equals the continuum flux.

Consider a continuum bath located on the x-axis at $x > 0$, with an absorbing boundary at $x = 0$. The bath is composed of an infinite number of independent noninteracting Brownian particles with average density ρ as $x \to \infty$, diffusing in a potential field $U(x)$. We assume that $U'(x) \to a > 0$ as $x \to \infty$, so that the steady state average density of particles is uniform at infinity.

In this setting, the motion of each particle is governed by the one-dimensional Langevin equation

$$\dot{x} = -\frac{dU}{dx} + \sqrt{2}\dot{w}, \tag{2.1}$$

where $w(t)$ is standard Brownian motion.

We assume the existence of a stationary concentration of bath particles, denoted $p(x)$. By assumption, the motions of different bath particles are independent, so the stationary concentration $p(x)$ satisfies the Nernst–Planck equation

$$\frac{d}{dx}\left[\frac{dp}{dx} + p\frac{dU}{dx}\right] = 0, \tag{2.2}$$

with the boundary conditions

$$p(0) = 0, \quad \text{and} \quad p(x) \to \rho \quad \text{as} \quad x \to \infty. \tag{2.3}$$

First, we modify the problem to that of a finite bath in the region $[0, L]$, with the boundary conditions

$$p(0) = 0, \quad p(L) = \rho.$$

The solution of the modified problem, denoted $p_L(x)$, is given by

$$p_L(x) = \rho \frac{e^{-U(x)} \displaystyle\int_0^x e^{U(s)}\, ds}{e^{-U(L)} \displaystyle\int_0^L e^{U(s)}\, ds}. \tag{2.4}$$

The steady state density of the infinite system $p(x)$, whenever it exists, is given as the limit

$$p(x) = \lim_{L\to\infty} p_L(x). \tag{2.5}$$

Under the given assumptions concerning the existence of a steady state density, the following limit exists:

$$0 < a^{-1} = \lim_{L\to\infty} \int_0^L e^{U(s)-U(L)} ds < \infty. \tag{2.6}$$

In this case, combining (2.6) with (2.5) and (2.4) gives

$$p(x) = \rho\, a\, e^{-U(x)} \int_0^x e^{U(s)} ds. \tag{2.7}$$

The continuum flux at the absorbing boundary is

$$J = -\left.\frac{dp\,(x)}{dx}\right|_{x=0} = -\rho a. \tag{2.8}$$

Note that the flux is negative as particles are flowing out of the bath, thus "decreasing" the number of bath particles.

In the next section we prove that when a steady state exists, the first arrival time from the continuum to the absorbing boundary is exponentially distributed, with a rate equal to the above flux (in absolute value), $\lambda = \rho a = |J|$. The proof that all subsequent interarrival times are also exponentially distributed with the same rate is postponed until section 5.

3. The probability law of the first arrival time. Before computing arrival times from an infinite continuum bath, we need a definition of a steady state infinite bath with an infinite number of discrete particles. We define an observation, or a measurement of the first arrival time from a steady state infinite bath, as follows. Following [4], at the start of observation, at time $t = 0$, we consider only the *finite* number of particles initially distributed in the interval $[0, L]$ of the infinite bath and compute the first arrival time of these particles. The first arrival time from the infinite bath is defined as the limit of the above arrival time when we let the length of the interval and the number of particles tend to infinity.

We denote by $N(L)$ the number of particles initially located in the interval $[0, L]$ and denote by $\tau(L)$ the first arrival time from this system. By definition, the time $\tau(L)$ is the *minimum* of the arrival times of all the $N(L)$ particles. Since the bath is in steady state and all diffusing particles are independent, the initial locations at time $t = 0$ of the $N(L)$ particles inside the finite region $[0, L]$, denoted $x_i(0)$ $(i = 1, \ldots, N(L))$, are i.i.d. random variables, distributed according to the steady state density $p(x)$ from (2.7) but normalized to the region $[0, L]$,

$$\Pr\Big\{x_i \in [x, x + dx]\Big\} = \frac{p(x)\, dx}{\displaystyle\int_0^L p(s)\, ds}. \tag{3.1}$$

By definition of the steady state particle concentration $p(x)$, it follows that the *average* number of particles inside the region $[0, L]$, denoted $E[N(L)]$, is given by

$$E\Big[N(L)\Big] = \int_0^L p(x)\, dx. \tag{3.2}$$

As is well known [6], $N(L)$, the total number of particles inside the region $[0, L]$, is a Poisson random variable whose average is $E[N(L)]$, as computed above in (3.2), and

its probability distribution function is

$$\Pr\Big\{N(L)=k\Big\}=\frac{E[N(L)]^k}{k!}\,e^{-E\left[N(L)\right]}. \tag{3.3}$$

To summarize so far, in our approximation scheme we consider only the finite number of particles in the infinite bath, initially confined to the interval $[0,L]$. This number of particles $N(L)$ follows the Poisson distribution (3.3), and the initial locations of the particles are i.i.d. random variables distributed according to (3.1).

Our purpose is to compute the probability law of the minimal arrival time to the origin of these $N(L)$ particles, sum over all possible values of $N(L)$ multiplied by their respective probabilities, and then take the limit as $L\to\infty$. Since the motions of different particles are independent of each other, for a bath with k particles

$$\Pr\Big\{\tau(L)>t\,|\,N(L)=k\Big\}=\Big[\Pr\big\{\tau_1>t\big\}\Big]^k, \tag{3.4}$$

where τ_1 denotes the first passage time (FPT) to the origin of a single particle initially distributed inside the region $[0,L]$. Combining (3.4) and (3.3), the FPT from the infinite bath, denoted τ, is given by

$$\begin{aligned}\Pr\Big\{\tau>t\Big\}&=\lim_{L\to\infty}\sum_{k=0}^{\infty}\Pr\Big\{\tau(L)>t\,|\,N(L)=k\Big\}\Pr\Big\{N(L)=k\Big\}\\&=\lim_{L\to\infty}\sum_{k=0}^{\infty}\Big[\Pr\big\{\tau_1>t\big\}\Big]^k\frac{E[N(L)]^k}{k!}\,e^{-E\left[N(L)\right]}\\&=\lim_{L\to\infty}\exp\Big\{-E\big[N(L)\big]\Big(1-\Pr\{\tau_1>t\}\Big)\Big\}.\end{aligned} \tag{3.5}$$

We denote by

$$G(x,t)=\Pr\{\tau_1>t\,|\,x\,(0)=x\}$$

the probability that a particle that starts out at x has not been absorbed by time t. It satisfies the partial differential equation [11]

$$\frac{\partial G}{\partial t}=\frac{\partial^2 G}{\partial x^2}-U'(x)\frac{\partial G}{\partial x}\qquad\text{for}\quad x>0, \tag{3.6}$$

with the boundary condition

$$G\,(0,t)=0$$

and the initial condition

$$G\,(x,0)=1\quad\text{for}\quad x>0.$$

According to (3.1) and (3.2), the FPT of a single particle is given by

$$\begin{aligned}\Pr\{\tau_1>t\}&=\int_0^L\Pr\Big\{x_i=x\Big\}G(x,t)dx\\&=\frac{\displaystyle\int_0^L p_L\,(x)\,G\,(x,t)\,dx}{E\Big[N(L)\Big]}.\end{aligned} \tag{3.7}$$

Inserting (3.7) and (3.2) into (3.5) gives

$$\Pr\Big\{\tau > t\Big\} = \exp\left\{ -\int_0^\infty p(x)\Big[1 - G(x,t)\Big]\,dx \right\}. \tag{3.8}$$

Using the abbreviation

$$F(t) = \int_0^\infty p(x)\Big[1 - G(x,t)\Big]\,dx,$$

we differentiate $F(t)$ with respect to t, interchange the order of integration (with respect to x) and differentiation, and use (3.6) to obtain

$$\begin{aligned} \frac{dF}{dt} &= -\int_0^\infty p(x)\left[-U'(x)\frac{\partial G}{\partial x} + \frac{\partial^2 G}{\partial x^2}\right] dx \\ &= -\int_0^\infty p(x)e^{U(x)}\frac{\partial}{\partial x}\left[e^{-U(x)}\frac{\partial G}{\partial x}\right] dx. \end{aligned} \tag{3.9}$$

Two integrations by parts yield the identity

$$\frac{dF}{dt} = -\,p(x)\frac{\partial G}{\partial x}\bigg|_0^\infty + Ge^{-U}\frac{d}{dx}\left(e^{U}p(x)\right)\bigg|_0^\infty - \int_0^\infty G(x)\frac{d}{dx}\left[e^{-U}\frac{d}{dx}\left(e^{U}p(x)\right)\right] dx.$$

Note that the integral vanishes due to (2.2). In addition, all contributions from the lower limit $x = 0$ vanish as both $G(0,t) = 0$ and $p(0) = 0$. Thus, we are left only with the contributions from the upper limit $x = \infty$,

$$\frac{dF}{dt} = \lim_{L\to\infty}\left\{ -p(L)\frac{\partial G}{\partial x}\bigg|_{x=L} + G\left(L,t\right)\left[U'(L)p\left(L\right) + \frac{dp}{dx}\bigg|_{x=L}\right]\right\}. \tag{3.10}$$

We separately estimate each term on the right-hand side of (3.10), starting with the last term. It follows from (2.2) and (2.8) that for all values of x

$$U'\left(x\right)p\left(x\right) + \frac{dp(x)}{dx} = -J.$$

Next, we consider the first term on the right-hand side of (3.10). The boundary condition (2.3) implies that

$$\lim_{L\to\infty} p(L) = \rho.$$

To compute the limit in (3.10) it remains to determine the asymptotic behavior of $G(x,t)$ and its spatial derivative, as $x \to \infty$. Obviously, by definition, for every fixed t, $G(x,t)$ is a monotone increasing function of x because it takes longer to reach the origin from a farther point. Similarly, it is obvious that the time to reach the origin from the point $x = L$ increases to infinity with L, so that for any finite t the probability of arriving at the origin from L *after* time t converges to 1 as $L \to \infty$. That is,

$$\lim_{L\to\infty} G(L,t) = 1.$$

Since $G(x,t)$ is a smooth function of x, it follows that

$$\lim_{L\to\infty} \left.\frac{\partial G}{\partial x}\right|_{x=L} = 0.$$

Thus, the first term on the right-hand side of (3.10) vanishes, and we obtain the result

$$\frac{dF}{dt} = -J. \tag{3.11}$$

Since $F(0) = 0$, one integration of (3.11) gives $F(t) = -Jt$. Inserting this result into (3.8) gives

$$\Pr\{\tau > t\} = \exp\{Jt\}, \tag{3.12}$$

which means that τ, the first arrival time from the continuum into the absorbing boundary, is exponentially distributed with rate $\lambda = -J$. Note that the probability law of the first arrival time from a steady state bath into the absorbing boundary depends on the profile of the potential $U(x)$ through only a single constant, the continuum flux J.

4. The first arrival time for steady state three-dimensional diffusion. To obtain an analogous result in three dimensions, we consider independently diffusing particles outside an arbitrary bounded domain Ω with a smooth boundary $\partial\Omega$ (see Figure 4.1). The particles in this three-dimensional bath are subjected to a potential field $-\nabla U(\boldsymbol{r})$ such that a steady state density $p(\boldsymbol{r})$ exists in the bath $\boldsymbol{R}^3 - \Omega$. It satisfies the differential equation

$$\mathcal{L}p(\boldsymbol{r}) = \nabla\cdot\Big(\nabla p(\boldsymbol{r}) + p(\boldsymbol{r})\nabla U(\boldsymbol{r})\Big) = -\nabla\cdot\mathcal{J}(\boldsymbol{r}) = 0, \quad \boldsymbol{r}\in\boldsymbol{R}^3 - \Omega, \tag{4.1}$$

where $\mathcal{J}(\boldsymbol{r})$ is the flux density vector.

We assume that $\nabla U(\boldsymbol{r})$ vanishes fast enough as $|\boldsymbol{r}|\to\infty$, so that the stationary density is uniform at infinity (see the appendix for details). We assume that a part of $\partial\Omega$, denoted $\partial\Omega_1$, is absorbing, and the remaining part, $\partial\Omega - \partial\Omega_1$, is reflecting.

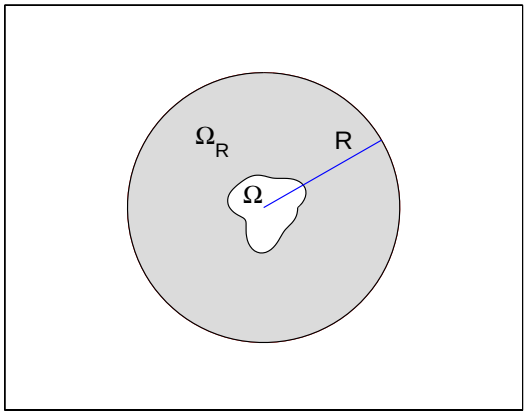

FIG. 4.1. *The domain Ω and its complement in the sphere Ω_R.*

Thus, the boundary conditions for the steady state density are an average density ρ at infinity,

$$\lim_{|\boldsymbol{r}|\to\infty} p\,(\boldsymbol{r}) = \rho, \tag{4.2}$$

absorption on $\partial\Omega_1$,

$$p(\boldsymbol{r})\Big|_{\partial\Omega_1} = 0,$$

and no flux boundary conditions on the reflecting part of the boundary, $\partial\Omega - \partial\Omega_1$,

$$\mathcal{J}\cdot\boldsymbol{\nu}\Big|_{\partial\Omega-\partial\Omega_1} = -\left(\nabla p + p\nabla U\right)\cdot\boldsymbol{\nu}\Big|_{\partial\Omega-\partial\Omega_1} = 0,$$

where $\boldsymbol{\nu}$ is the unit outer normal at the boundary.

As in the previous section, we start our analysis from a large ball of radius R denoted Ω_R, centered at the origin, such that $\Omega \subset \Omega_R$ (see Figure 4.1). We place in $\Omega_R - \Omega$ a finite number of particles $N(R)$, initially located according to the steady state density $p(\boldsymbol{r})$ normalized to the ball Ω_R,

$$\Pr\Big\{\boldsymbol{r}_i \in \boldsymbol{r} + d\boldsymbol{r}\Big\} = \frac{p(\boldsymbol{r})\,d\boldsymbol{r}}{\displaystyle\int_{\Omega_R-\Omega} p(\boldsymbol{y})d\boldsymbol{y}}.$$

As in the one-dimensional case, the total number of particles $N(R)$ is a Poisson distributed random variable with average

$$E\big[N(R)\big] = \int_{\Omega_R-\Omega} p\,(\boldsymbol{y})\;d\boldsymbol{y}.$$

In analogy to (3.5) for the one-dimensional case, the first arrival time from the continuum bath into the absorbing boundary $\partial\Omega_1$ is given by

$$\Pr\Big\{\tau > t\Big\} = \lim_{R\to\infty} \exp\Big\{-E[N(R)]\Big(1 - \Pr\big\{\tau_1 > t\big\}\Big)\Big\}, \tag{4.3}$$

where τ_1 denotes the first arrival time of a single particle from the ball Ω_R to the absorbing boundary.

We follow the same steps of computation as in the one-dimensional case. We denote by

$$G(\boldsymbol{r},t) = \Pr\Big\{\tau_1 > t \,|\, \boldsymbol{r}\,(0) = \boldsymbol{r}\Big\}$$

the probability that a diffusing particle will arrive at $\partial\Omega_1$ after time t, starting from an initial position $\boldsymbol{r}$ at time $t = 0$. Then $G\,(\boldsymbol{r},t)$ satisfies the evolution equation [11]

$$\frac{\partial G\,(\boldsymbol{r},t)}{\partial t} = \mathcal{L}^* G\,(\boldsymbol{r},t) = \nabla\cdot\nabla G\,(\boldsymbol{r},t) - \nabla G\,(\boldsymbol{r},t)\cdot\nabla U, \tag{4.4}$$

where $\mathcal{L}^*$ is the backward operator (the formal adjoint to $\mathcal{L}$ in (4.1)). The boundary conditions for $G(\boldsymbol{r},t)$ are

$$G\,(\boldsymbol{r},t)\Big|_{\partial\Omega_1} = 0,$$

$$\nabla G(\boldsymbol{r},t)\cdot\boldsymbol{\nu}\Big|_{\partial\Omega-\partial\Omega_1} = 0,$$

and the initial condition is

$$G(\boldsymbol{r},0)=1 \qquad \text{for } \boldsymbol{r}\in \boldsymbol{R}^3-\Omega.$$

The quantity of interest, the probability law of τ_1, is given by

$$\Pr\Big\{\tau_1>t\Big\}=\frac{\displaystyle\int_{\Omega_R-\Omega} p(\boldsymbol{r})\,G(\boldsymbol{r},t)\;d\boldsymbol{r}}{\displaystyle\int_{\Omega_R-\Omega} p(\boldsymbol{r})\,d\boldsymbol{r}}. \tag{4.5}$$

Repeating the same steps as in the one-dimensional computation leads to the formula

$$\begin{aligned}\Pr\Big\{\tau>t\Big\}&=\lim_{R\to\infty}\exp\Big\{-\int_{\Omega_R-\Omega}p(\boldsymbol{r})\Big[1-G(\boldsymbol{r},t)\Big]\,d\boldsymbol{r}\Big\}\\ &=\lim_{R\to\infty}\exp\Big\{F_R(t)\Big\}.\end{aligned} \tag{4.6}$$

Differentiating $F_R(t)$ with respect to t and using (4.4) gives

$$\frac{dF_R}{dt}=\int_{\Omega_R-\Omega}p(\boldsymbol{r})\mathcal{L}^*G(\boldsymbol{r},t)\,d\boldsymbol{r}.$$

Since $\mathcal{L}p(\boldsymbol{r})=0$, we can equivalently write

$$\frac{dF_R}{dt}=\int_{\Omega_R-\Omega}\Big[p\mathcal{L}^*G-G\mathcal{L}p\Big]\,d\boldsymbol{r}. \tag{4.7}$$

Inserting the expressions for the operators $\mathcal{L}$ and $\mathcal{L}^*$ from (4.1) and (4.4), respectively, into (4.7) yields

$$\int_{\Omega_R-\Omega}\Big[p\mathcal{L}^*G-G\mathcal{L}p\Big]d\boldsymbol{r}=\int_{\Omega_R-\Omega}\Big[p\Delta G-G\Delta p\Big]\,d\boldsymbol{r}-\int_{\Omega_R-\Omega}\nabla\cdot\Big[G\,p\nabla U\Big]\,d\boldsymbol{r}.$$

Applying Green's second identity to the first integral and the divergence theorem to the second integral, we obtain

$$\begin{aligned}\frac{dF_R}{dt}&=\oint_{\partial[\Omega_R-\Omega]}[p\nabla G-G\nabla p-Gp\nabla U]\cdot d\boldsymbol{S}\\ &=\oint_{\partial[\Omega_R-\Omega]}[p\nabla G+\mathcal{J}\,G]\cdot d\boldsymbol{S},\end{aligned} \tag{4.8}$$

where $d\boldsymbol{S}$ is a surface differential multiplied by a unit vector in the direction normal to the surface.

Consider first the contribution from the boundary $\partial\Omega$. On the absorbing boundary $\partial\Omega_1$, both $G(\boldsymbol{r},t)$ and $p(\boldsymbol{r})$ vanish, so there is no contribution to the surface integral from this region. On the remaining part, $\partial\Omega-\partial\Omega_1$, the boundary conditions are $\nabla G=0$ and $\mathcal{J}=0$, so once again there is zero contribution to the surface integral. Thus, we retain only the contribution from the far boundary $\partial\Omega_R$. On this boundary, at any finite time t,

$$\lim_{R\to\infty}G(\boldsymbol{r},t)\Big|_{|\boldsymbol{r}|=R}=1, \qquad \lim_{R\to\infty}\nabla G(\boldsymbol{r},t)\Big|_{|\boldsymbol{r}|=R}=0, \tag{4.9}$$

and the convergence is exponentially fast (see the appendix). Thus, combining (4.9) with (4.8), the contribution from the boundary $\partial\Omega_R$ can be approximated by

$$\frac{dF_R}{dt} = \int_{\partial\Omega_R} \mathcal{J}(\boldsymbol{r}) \cdot d\boldsymbol{S} + o(1) \quad \text{for} \quad R \gg 1. \tag{4.10}$$

Recall from (4.1) that $\nabla \cdot \mathcal{J}(\boldsymbol{r}) = 0$. Thus, using the divergence theorem,

$$0 = \int_{\Omega_R - \Omega} \nabla \cdot \mathcal{J}(\boldsymbol{r})\, d\boldsymbol{r} = \oint_{\partial\Omega_R} \mathcal{J} \cdot d\boldsymbol{S} - \oint_{\partial\Omega} \mathcal{J} \cdot d\boldsymbol{S},$$

or equivalently,

$$\oint_{\partial\Omega_R} \mathcal{J} \cdot d\boldsymbol{S} = \oint_{\partial\Omega} \mathcal{J} \cdot d\boldsymbol{S} = J, \tag{4.11}$$

where J denotes the *total* continuum flux on the boundary $\partial\Omega$. Combining (4.11) and (4.10) and integrating with respect to t gives

$$\lim_{R\to\infty} F_R(t) = Jt. \tag{4.12}$$

Equations (4.12) and (4.6) mean that the first arrival time from the bath to the absorbing boundary is exponentially distributed with a rate that equals the continuum flux predicted from the steady state solution of the Nernst–Planck equation. Note that the total flux J is negative due to the fact that particles are exiting the bath and entering the absorbing boundary of Ω.

5. The next arrival times. So far, we have shown that the *first* arrival time of a particle from the continuum bath to the absorbing boundary is exponentially distributed. Now, we follow the analysis of [7] to show that *all* interarrival times are exponentially distributed with the same rate.

As above, we first consider a bath with $N(R)$ particles initially distributed in $\Omega_R - \Omega$, calculate the PDF of the second arrival time, and then let $R \to \infty$. We denote by $t_1(R)$ and $t_2(R)$ the first and second arrival times into $\partial\Omega_1$ from the finite system, and by t_1 and t_2 the corresponding arrival times from the infinite continuum bath. Obviously, for $t > s$

$$\Pr\Big\{t_2 > t \,|\, t_1 = s\Big\} = \lim_{R\to\infty} \Pr\Big\{t_2(R) > t \,|\, t_1(R) = s\Big\}.$$

For a bath with a finite number of particles, we have

$$\begin{aligned}
&\Pr\Big\{t_2(R) > t \,|\, t_1(R) = s\Big\} \\
&\quad = \sum_{k=1}^{\infty} \Pr\Big\{\{t_2(R) > t \,|\, t_1(R) = s\} \,\Big|\, N(R) = k\Big\} \Pr\Big\{N(R) = k\Big\} \\
&\quad = \sum_{k=1}^{\infty} \frac{\Pr\big\{t_2(R) > t \cap t_1(R) = s \,|\, N(R) = k\big\}}{\Pr\big\{t_1(R) = s \,|\, N(R) = k\big\}} \Pr\Big\{N(R) = k\Big\}.
\end{aligned}$$

Since all diffusing particles are independent,

$$\Pr\big\{t_2(R) > t \cap t_1(R) = s \,|\, N(R) = k\big\} = \binom{k}{1} \Pr\big\{\tau_1 = s\big\} \Pr\big\{\tau_1 > t\big\}^{k-1},$$

which means that there are k possibilities from which to choose the specific particle that arrives first, at time s, and then all remaining $k-1$ particles must arrive later than time t. Similarly,

$$\Pr\{t_1(R)=s\,|\,N(R)=k\}=\begin{pmatrix}k\\1\end{pmatrix}\Pr\{\tau_1=s\}\Pr\{\tau_1>s\}^{k-1}.$$

Combining the last three equations gives

$$\Pr\Big\{t_2(R)>t\,|\,t_1(R)=s\Big\}=\sum_{k=1}^{\infty}\frac{\Pr\{\tau_1>t\}^{k-1}}{\Pr\{\tau_1>s\}^{k-1}}\Pr\{N(R)=k\}. \tag{5.1}$$

Inserting the Poisson distribution of $N(R)$ into (5.1) simplifies the right-hand side to

$$\begin{aligned}\Pr\Big\{t_2(R)>t\,|\,t_1(R)=s\Big\}&=\frac{\Pr\{\tau_1>s\}}{\Pr\{\tau_1>t\}}\sum_{k=1}^{\infty}\left(\frac{E[N(R)]\Pr\{\tau_1>t\}}{\Pr\{\tau_1>s\}}\right)^k\frac{e^{-E[N(R)]}}{k!}\\&=\frac{\Pr\{\tau_1>s\}}{\Pr\{\tau_1>t\}}e^{-E[N(R)]}\left(\exp\left\{\frac{E[N(R)]\Pr\{\tau_1>t\}}{\Pr\{\tau_1>s\}}\right\}-1\right).\end{aligned} \tag{5.2}$$

According to (4.6) and (4.3) we have

$$F_R(t)=E[N(R)]\Pr\{\tau_1<t\},$$

which further simplifies the right-hand side of (5.2) to

$$\frac{\Pr\{\tau_1>s\}}{\Pr\{\tau_1>t\}}\left\{\exp\left(\frac{F_R(s)-F_R(t)}{\Pr\{\tau_1>s\}}\right)-\exp\Big(-E[N(R)]\Big)\right\}. \tag{5.3}$$

We now take the limit as $R\to\infty$. According to (4.5), the distribution of the FPT of a single particle is

$$\lim_{R\to\infty}\Pr\{\tau_1>t\}=\lim_{R\to\infty}\frac{\displaystyle\int_{\Omega_R-\Omega}p(\boldsymbol{r})G(\boldsymbol{r},t)\,d\boldsymbol{r}}{\displaystyle\int_{\Omega_R-\Omega}p(\boldsymbol{r})}.$$

According to (4.9), for any finite time t, as $|r|\to\infty$, $G(\boldsymbol{r},t)\to 1$. Also, according to (4.2), $p(\boldsymbol{r})\to\rho$ as $|\boldsymbol{r}|\to\infty$. Therefore,

$$\lim_{R\to\infty}\Pr\{\tau_1>t\}=1.$$

Obviously, for $R\to\infty$, $E[N(R)]\to\infty$, so the last term in (5.3) vanishes. Finally, according to (4.12), $F_R(t)\to Jt$ as $R\to\infty$. Therefore,

$$\Pr\Big\{t_2>t\,|\,t_1=s\Big\}=\exp\left(J(t-s)\right).$$

That is, the interarrival time between the first and second particle depends only on the *elapsed* time $t-s$ since the first arrival at time s, and is independent of the first arrival time s. Moreover, this interarrival time is exponentially distributed with the same rate $\lambda=-J$, which is equal to the Smoluchowski flux.

In a similar manner, one can show that all interarrival times are exponentially distributed, rendering the arrivals a memoryless Poisson process.

6. Summary and discussion. Diffusion of independent (noninteracting) particles is an approximation widely used to describe the motion of ions in solution. Such an approximation represents a coarse-grained description of the effective motion of ions. It is used in the physical chemistry of electrolytic solutions, where solutions are described in terms of an electrochemical potential and interactions are replaced by an activity coefficient. In this approximation, ionic concentrations satisfy the Nernst–Planck equation, that is, Fickian diffusion and transport in a mean field. The underlying microscopic (Einsteinian) scenario for this description is the Brownian motion of noninteracting individual particles that interact only with a nonfluctuating mean field.

In simulations of ions in solution [12], [13], [14], [15], [16], [17], [18], [19], [20], [21], [22], [23], especially in the context of molecular biophysics [24], [25], [26], a small scale simulation has to be connected to the surrounding continuum. The interactions between the ions inside the simulation volume and their interactions with the far field of the surrounding continuum can be taken into account inside the simulation volume. Ions have to be introduced into the simulation volume and removed from it in a fashion consistent with their motion in the continuum. The exchange of ions between the discrete simulation volume and the surrounding continuum is a sorely missed link in the theory of ionic simulations. The exchange law is often *assumed* rather than computed from the assumed physical laws governing ions in solution [27], [28], [29], [30].

Two ionic species can be distinguished in a simulation of a discrete volume surrounded by a continuum: (i) the species of ions that have not been in the simulation so far and (ii) the species of ions that have left the simulation into the continuum. The latter recirculate in and out of the simulation at random times. In this paper, we have considered species (i) of ions that enter the simulation for the first time. They arrive at the simulation from a continuum, where they are described by physical chemistry as independent (noninteracting) Brownian particles that interact only with a mean field. Once they reach the simulation volume for the first time their species change to type (ii). This means that they are absorbed permanently in the boundary of the simulation volume (as ions of species (i)). When they re-emerge from the simulation volume they are no longer of species (i) but rather are permanently of species (ii). Thus the boundary of the simulation volume is absorbing for the diffusion process of species (i) in the continuum.

In this paper, we have established that the absorption stream of species (i) is Poissonian with rate equal to the absorption flux calculated from classical continuum diffusion theory. That is, the interarrival times of ions of species (i) to the absorbing boundary are i.i.d. exponential random variables. This result means that the process of introducing new ions into the simulation has no memory, and thus no record of previous arrivals has to be kept. This property simplifies considerably the time course of the simulation.

Yet another application of our results is to ionic permeation through protein channels. In barrier models of ionic permeation through protein channels [31], transitions between the possible states of an ion inside and outside the channel are assumed Markovian. This implies that times between transitions have to be exponentially distributed. Our result shows that the transition times from the continuum into the channel are indeed exponentially distributed. The transitions times inside a channel are in general not exponential because there are usually no high barriers for the diffusive motion of the ion to overcome.

Realistic simulations of ionic permeation in protein channels, be it molecular dynamics or Langevin dynamics, must connect the simulation volume to the surrounding continuum because both ends of biological membrane channels are connected to salt water baths. The present computation, though not a full description of such a simulation, is the first step toward the development of these simulations. Further steps in this development will be described in separate papers.

Appendix. We consider a smooth field $\nabla U(\boldsymbol{r})$ in $\boldsymbol{R}^3$ such that

$$|\boldsymbol{r}|\,|\nabla U(\boldsymbol{r})| = O(1) \quad \text{as} \quad |\boldsymbol{r}| \to \infty. \tag{A.1}$$

We denote by $G(\boldsymbol{r},t)$ the solution of the initial boundary value problem

$$\frac{\partial G(\boldsymbol{r},t)}{\partial t} = \Delta G(\boldsymbol{r},t) - \nabla U(\boldsymbol{r}) \cdot \nabla G(\boldsymbol{r}\ ,t)$$

in $\boldsymbol{R}^3 - \Omega$, where Ω is a smooth bounded domain in $\boldsymbol{R}^3$. We assume that $G(\boldsymbol{r},t)$ satisfies a homogeneous boundary condition on $\partial\Omega$, that is, an absorbing condition on a portion $\partial\Omega_1$ of $\partial\Omega$ and a reflecting condition on $\partial\Omega - \partial\Omega_1$. The initial condition for $G(\boldsymbol{r},t)$ is

$$G(\boldsymbol{r},0) = 1.$$

We show that for each fixed t

$$G(\boldsymbol{r},t) \to 1 \quad \text{as} \quad |\boldsymbol{r}| \to \infty,$$

with convergence at an exponential rate. First, we write

$$G(\boldsymbol{r},t) = \int_{\boldsymbol{R}^3-\Omega} P(\boldsymbol{y},t\,|\,\boldsymbol{r})\ d\boldsymbol{y},$$

where $P(\boldsymbol{y},t\,|\,\boldsymbol{r})$ is the solution of the adjoint problem

$$\frac{\partial P(\boldsymbol{y},t\,|\,\boldsymbol{r})}{\partial t} = \Delta_{\boldsymbol{y}} P(\boldsymbol{y},t\,|\,\boldsymbol{r}) + \nabla_{\boldsymbol{y}} \cdot \left[\nabla_{\boldsymbol{y}} U(\boldsymbol{y})\, P(\boldsymbol{y},t\,|\,\boldsymbol{r})\right] \tag{A.2}$$

in $\boldsymbol{R}^3 - \Omega$, with the mixed absorbing and no flux boundary conditions on $\partial\Omega_1$ and $\partial\Omega - \partial\Omega_1$, respectively. The initial condition for $P(\boldsymbol{y},t\,|\,\boldsymbol{r})$ is

$$P(\boldsymbol{y},0\,|\,\boldsymbol{r}) = \delta(\boldsymbol{y}-\boldsymbol{r}).$$

For large $\boldsymbol{r}$, we introduce the scaling $\boldsymbol{y} = R\boldsymbol{\eta}$, $\boldsymbol{r} = R\boldsymbol{\xi}$, $t = R^2\tau$, $U(\boldsymbol{y}) = V(\boldsymbol{\eta})$, and $P(\boldsymbol{y},t\,|\,\boldsymbol{r}) = Q(\boldsymbol{\eta},\tau\,|\,\boldsymbol{\xi})$. Then (A.2) takes the form

$$\frac{\partial Q(\boldsymbol{\eta},\tau\,|\,\boldsymbol{\xi})}{\partial \tau} = \Delta_{\boldsymbol{\eta}} Q(\boldsymbol{\eta},\tau\,|\,\boldsymbol{\xi}) + \nabla_{\boldsymbol{\eta}} \cdot \left[\nabla_{\boldsymbol{\eta}} V(\boldsymbol{\eta})\, Q(\boldsymbol{\eta},\tau\,|\,\boldsymbol{\xi})\right]$$

with the initial condition

$$Q(\boldsymbol{\eta},0\,|\,\boldsymbol{\xi}) = \frac{1}{R^3}\delta(\boldsymbol{\eta}-\boldsymbol{\xi}).$$

For large R the domain Ω shrinks to nearly a point at the origin. For fixed t and large R the scaled time τ becomes small. According to (A.1), we have

$$\nabla_{\boldsymbol{\eta}} V(\boldsymbol{\eta}) = O(1) \quad \text{as} \quad R \to \infty.$$

It follows from [32] that for small τ

$$Q(\boldsymbol{\eta},\tau\,|\,\boldsymbol{\xi}) \sim \frac{1}{R^3\,(4\pi\tau)^{3/2}} \exp\left\{-\frac{|\boldsymbol{\eta}-\boldsymbol{\xi}|^2}{4\tau}\right\}.$$

Scaling back to the original variables, we find that for large $|\boldsymbol{r}|$

$$P(\boldsymbol{y},t\,|\,\boldsymbol{r}) \sim \frac{1}{(4\pi t)^{3/2}} \exp\left\{-\frac{|\boldsymbol{y}-\boldsymbol{r}|^2}{4t}\right\}.$$

Writing

$$\begin{aligned} G(\boldsymbol{r},t) &= \int_{\boldsymbol{R}^3-\Omega} P(\boldsymbol{y},t\,|\,\boldsymbol{r})\; d\boldsymbol{y} \\ &\sim \frac{1}{(4\pi t)^{3/2}} \int_{\boldsymbol{R}^3} \exp\left\{-\frac{|\boldsymbol{y}-\boldsymbol{r}|^2}{4t}\right\} d\boldsymbol{y} - \frac{1}{(4\pi t)^{3/2}} \int_{\Omega} \exp\left\{-\frac{|\boldsymbol{y}-\boldsymbol{r}|^2}{4t}\right\} d\boldsymbol{y} \\ &= 1 - \frac{1}{(4\pi t)^{3/2}} \int_{\Omega} \exp\left\{-\frac{|\boldsymbol{y}-\boldsymbol{r}|^2}{4t}\right\} d\boldsymbol{y}, \end{aligned}$$

we estimate

$$\int_{\Omega} \exp\left\{-\frac{|\boldsymbol{y}-\boldsymbol{r}|^2}{4t}\right\} d\boldsymbol{y} \le |\Omega| \exp\left\{-\frac{|\mathrm{dist}\,(\Omega,\boldsymbol{r})|^2}{4t}\right\},$$

where $\mathrm{dist}(\Omega,\boldsymbol{r})$ denotes the distance from the point $\boldsymbol{r}$ to Ω. This now proves the assertion. □

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