Variational bounds for first-passage-time problems in stratified porous media

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We examine the first-passage-time problem for passive tracer transport in flow through porous media. The simplified model used [G. Matheron and G. de Marsily, Water Resources Res. **16**, 901 (1980)] pertains especially to groundwater flow, and assumes that the medium is fully stratified. Transport normal to the layering is governed by diffusion alone; transport parallel to the layering is governed by both diffusion and convection. The fluid velocity varies randomly from layer to layer. The region of interest is vertically infinite but horizontally finite (of length $2L$), with a source inside and sinks on the boundaries. We average a path-integral expression for the Green function over velocity fluctuations and approximate the result in the limits of long distance and long time via Feynman's variational method. We calculate the exit time distribution and the mean first passage time. The latter is proportional to $L^{4/3}$, consistent with previous work.

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I. INTRODUCTION

Transport of a passive tracer through a porous medium by a fluid is a problem common to several fields of applied physics, including filtration processes and groundwater hydrology [1]. The problem is often well understood over regions typically of the order of centimeters, where the medium is treated as a *homogeneous* continuum with certain bulk properties, and where laws governing transport through the medium are known. The problem is not so well understood over regions typically of the order of meters, where we do not know the large-scale transport laws. To find these laws, we treat a large-scale region as an aggregation of smaller subregions, i.e., a *heterogeneous* continuum. Transport through the large region can be described by a local version of the smaller-scale transport equation. Averaging over the heterogeneities results in an equivalent homogeneous description good over large length scales. The heterogeneities are modeled as random functions of position. It is usually assumed that the central limit theorem (CLT) holds, i.e., that if in the limit of long times a tracer particle samples a statistically representative set of the fluctuating values, then the distribution of particle displacements is Gaussian, and the particle's mean square displacement increases as the first power of time t (diffusion) [2]. If the values sampled by the tracer are not representative, then the distribution is not generally Gaussian and the mean square displacement increases as t^{α}, where α may be less than 1 (subdiffusion) or greater than 1 (superdiffusion) [3,4]. The most common way of obtaining an effective averaged description is through a perturbation expansion in powers of the fluctuations. The perturbation approach has proven to be highly successful, but it has its limitations, two of the more important being that the calculations necessary for higher-order terms are very difficult, and that the applicability of the perturbation approach is limited to systems with weak fluctuations.

Interest in groundwater flow leads quite naturally to interest in flow through layered media, given that rock and sediment are so often found to be layered. Since velocity of flow can be obtained as a function of permeability from Darcy's law and the incompressibility condition, fluctuations in permeability such as occur in layered media will induce fluctuations in velocity. These latter, in turn, will induce enhanced dispersion of a passive tracer released into the flow. Generally, theoretical investigations assume that the medium is of infinite extent, and consider the mean tracer concentration to be the prime object of interest. This is mathematically convenient in that one is not obliged to work with boundaries which are a finite distance from the source, but it is unusual for an experiment to be so arranged. A more common experimental practice is to inject tracer into the medium at one point, and then to measure the time interval necessary for the tracer to reach the boundary of the medium. This "first-passage-time" problem has been well studied in one dimension [5,2,6], and is now being studied in more complex media [7].

We will examine the first-passage-time problem for flow through a layered medium. Transport normal to the layering is governed by diffusion; transport parallel to the velocity is governed by both diffusion and convection, with the velocity a random function of transverse position; and transport parallel to the layering but normal to the velocity is simple diffusion, which we shall ignore. The dispersion tensor is known to be anisotropic, with principal directions parallel to and normal to flow; however, since convective transport dominates diffusive transport parallel to bulk flow in the limit of long times, we can take the parallel and transverse dispersion coefficients to be numerically equal. This will simplify the equations somewhat. This model is of theoretical interest because the average concentration profile in unbounded space is superdiffusive [8]. The anomalous behavior arises from the interplay between convection and diffusion, which induces long range time correlations in the velocity fluctuations [9,10,4]; while more and more of the velocity distribution is sampled as time increases, the distribution is never sampled completely, and the sampled velocity values are not independent. We will assume that the mean flow is zero (center of mass frame), that the region of interest is bounded by absorbing walls (sinks) oriented normal to the flow, and that the tracer is released halfway between the two walls. While the tracer has a finite distance it can travel parallel to the flow, it also has an indefinitely large distance it can travel normal to the flow, and an indefinitely large number of layers it can visit. The usual experimental apparatus is not actually of infinite thickness, but it can be effectively so if the characteristic time necessary to leave the system by moving parallel to the flow is much less than the characteristic time necessary to leave the system by diffusing normal to the flow.

We use Feynman's variational method [11,12] to approximate the average Green function; from the result we calculate the exit time distribution and the mean first passage time. Given our assumptions, the exit time distribution is proportional to $(t^{1/2}/L^2)\exp\{-\gamma t^{3/2}/L^2\}$, with γ some constant dependent on problem parameters; it follows from this that the mean first passage time is proportional to $L^{4/3}$.

II. PROBLEM

The mass concentration of tracer in the fluid $c(\mathbf{r},t)$ is governed by a convection-diffusion equation (CDE)

$$\left[\frac{\partial}{\partial t}+\mathbf{u}(\mathbf{r})\cdot\nabla-D\nabla^2\right]c(\mathbf{r},t)=0\ . \tag{1}$$

We take the layering to be parallel to $\hat{\mathbf{x}}$. If we apply a pressure gradient parallel to the layering, then the velocity $\mathbf{u}(\mathbf{r})$ is parallel to $\hat{\mathbf{x}}$ and a random function of y alone, $\mathbf{u}(\mathbf{r})=u(y)\hat{\mathbf{x}}$, which follows from Darcy's law [1], supplemented by an assumption that the permeability tensor is diagonal. We assume that the velocity fluctuations can be characterized as Gaussian white noise, with the statistics of $u(y)$ completely determined by $\langle u(y)\rangle=0$ and $\langle u(y)u(y')\rangle=\rho(|y-y'|)=\sigma^2\delta(y-y')$. D is the unperturbed diffusion coefficient. The boundary conditions are $c(\mathbf{r},t)=0$ at $x=\pm L$, and as $y\to\pm\infty$ (see Fig. 1). The Green function $G(\mathbf{r},t;\mathbf{r}_0,t_0)$ for Eq. (1), defined by

$$\left[\frac{\partial}{\partial t}+\mathbf{u}(\mathbf{r})\cdot\nabla-D\nabla^2\right]G(\mathbf{r},t;\mathbf{r}_0,t_0)=\delta(\mathbf{r}-\mathbf{r}_0)\delta(t-t_0)\ , \tag{2}$$

is no more than the probability that a tracer particle starting at $(\mathbf{r}_0,t_0)$ will end up at $(\mathbf{r},t)$. The exit time distribution $p(t,\mathbf{r}_0,t_0)$ is defined as the probability per unit

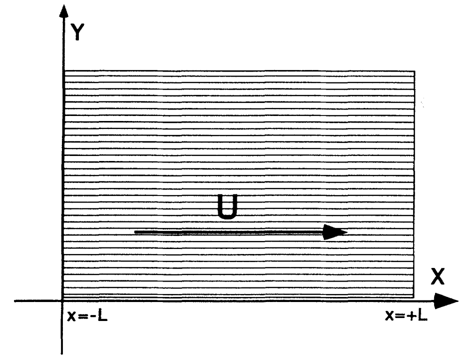

FIG. 1. Geometry of layered medium for first-passage-time problem.

time that the particle leaves the region of interest at time t, and is given in terms of the Green function by

$$p(t,\mathbf{r}_0,t_0)=-\frac{\partial}{\partial t}\int_{-L}^{+L}dx\int_{-\infty}^{+\infty}dy\ G(\mathbf{r},t;\mathbf{r}_0,t_0)\ . \tag{3}$$

The mean first passage time $T(\mathbf{r}_0)$ is defined as

$$T(\mathbf{r}_0)\equiv\int_{t_0}^{+\infty}dt(t-t_0)p(t,\mathbf{r}_0,t_0)\ . \tag{4}$$

One can obtain an equation for $T(\mathbf{r})$ from Eq. (2) [6]:

$$D\nabla^2T(\mathbf{r})+\mathbf{u}(\mathbf{r})\cdot\nabla T(\mathbf{r})+1=0\ . \tag{5}$$

Usually, Eq. (5) would be preferred to Eq. (1), for the obvious reasons of fewer variables and fewer derivatives, but we will not make use of Eq. (5). Our unperturbed system is governed by pure diffusion in the x direction, so that $T_0\sim L^2$. For the averaged system, the simplest naive argument [13] gives $\langle T\rangle\sim L^{4/3}$, while a more refined argument based on crossover scaling due to Redner [14] gives $\langle T\rangle\sim(L\ln L)^{4/3}$. Also, we are interested in large L. It is difficult to see how one might perturb about $T_0\sim L^2$, and reach $\langle T\rangle\sim L^{4/3}$ for large L, as the unperturbed quantity would dominate the expected averaged quantity in the parameter range of interest. Furthermore, from a perturbation expansion, one can readily see that the first order correction scales as L^3. This indicates that perturbative methods are best limited to cases for which L is small and the fluctuations are weak. Though we therefore desire a nonperturbative calculation, we do not know of a nonperturbative technique which can be applied immediately to Eq. (5) [15]. On the other hand, such techniques do exist for Eq. (1).

Since the variational method is based on path integrals, the first task is to obtain a path-integral version of the problem. To start, we need the solution to Eq. (2) in the special case that the velocity is a nonzero constant u_0. This solution can be obtained using images, as is familiar from elementary electrostatics:

$$G(\mathbf{r}_N,t_N;\mathbf{r}_0,t_0)=\frac{1}{4\pi D(t_N-t_0)}\exp\left\{-\frac{(y_N-y_0)^2}{4D(t_N-t_0)}\right\}$$
$$\times\sum_{n=-\infty}^{+\infty}(-1)^n\exp\left\{\frac{u_0}{D}\left[nL+\frac{[-1+(-1)^n]x_0}{2}\right]\right.$$
$$\left.-\frac{1}{4D(t_N-t_0)}[x_N-2nL-(-1)^n x_0-u_0(t_N-t_0)]^2\right\}. \tag{6}$$

This can be rewritten using the integral identity

$$\frac{1}{(2\pi M)^{1/2}}\exp\left\{-\frac{z^2}{2M}\right\}=\int_{-\infty}^{+\infty}\frac{dp}{2\pi}\exp\{-\tfrac{1}{2}Mp^2+ipz\} \tag{7}$$

so that

$$G(\mathbf{r}_N,t_N;\mathbf{r}_0,t_0)=\frac{1}{[4\pi D(t_N-t_0)]^{1/2}}\exp\left\{-\frac{(y_N-y_0)^2}{4D(t_N-t_0)}\right\}$$
$$\times\int_{-\infty}^{+\infty}\frac{dp}{2\pi}\sum_{n=-\infty}^{+\infty}(-1)^n\exp\left\{\frac{u_0}{D}\left[nL+\frac{[-1+(-1)^n]x_0}{2}\right]-D(t_N-t_0)p^2\right.$$
$$\left.+ip[x_N-2nL-(-1)^n x_0-u_0(t_N-t_0)]\right\}. \tag{8}$$

This is sometimes called the momentum representation of Eq. (6). To obtain the concentration with fluctuating parameters, we divide the time interval into N equal segments, of length $\Delta t=(t_N-t_0)/N$. Then any particular path $\mathbf{r}(t)$ from $(\mathbf{r}_0,t_0)$ to $(\mathbf{r}_N,t_N)$ can be approximated by $N+1$ points $(\mathbf{r}_k\equiv\mathbf{r}(t_k),\ t_k\equiv t_0+k\Delta t)$, where $0\le k\le N$. The probability of going from $(\mathbf{r}_k,t_k)$ to $(\mathbf{r}_{k+1},t_{k+1})$ can be found from Eq. (8) by replacing $N\to k+1$, $0\to k$, $p\to p_k$, $n\to n_k$, and $u_0\to u(y_{k+1})$. We choose $u(y_{k+1})$ so that the path-integral expression we eventually obtain obeys Eq. (2) (cf. Appendix). The probability of taking a particular path is the product of the probabilities of taking each link in the path, and the total probability of going from $(\mathbf{r}_0,t_0)$ to $(\mathbf{r}_N,t_N)$ is obtained by summing this last quantity over all possible paths. The result is

$$G(\mathbf{r}_N,t_N;\mathbf{r}_0,t_0)=\prod_{j=1}^{N-1}\int dx_j dy_j\prod_{k=0}^{N-1}\int\frac{dp_k}{2\pi}\prod_{l=0}^{N-1}\sum_{n_l=-\infty}^{+\infty}(-1)^{n_l}\frac{1}{(4\pi D\Delta t)^{N/2}}$$
$$\times\exp\left\{-\sum_{m=0}^{N-1}\frac{(y_{m+1}-y_m)^2}{4D\Delta t}\right.$$
$$+\sum_{m=0}^{N-1}\left[\frac{u(y_{m+1})}{D}\left[n_mL+\frac{[-1+(-1)^{n_m}]x_m}{2}\right]\right.$$
$$-D\Delta t p_m^2+ip_m[x_{m+1}-2n_mL-(-1)^{n_m}x_m$$
$$\left.\left.-u(y_{m+1})\Delta t]\right]\right\}. \tag{9}$$

We use the momentum representation because the function in the exponent is linear in the velocity, which makes averaging much easier. Averaging over fluctuations in velocity [16] gives

$$\begin{aligned}
&\langle G(\mathbf{r}_N,t_N;\mathbf{r}_0,t_0)\rangle \\
&=\int Du \exp\left\{-\tfrac{1}{2}\int dy\, dy'\rho^{-1}(|y-y'|)u(y)u(y')\right\}G(\mathbf{r}_N,t_N;\mathbf{r}_0,t_0) \\
&=\prod_{j=1}^{N-1}\int dx_j dy_j \prod_{k=0}^{N-1}\int \frac{dp_k}{2\pi}\prod_{l=0}^{N-1}\sum_{n_l=-\infty}^{+\infty}(-1)^{n_l}\frac{1}{(4\pi\Delta t)^{N/2}} \\
&\qquad\times\exp\left\{-\sum_{m=0}^{N-1}\frac{(y_{m+1}-y_m)^2}{4D\Delta t}\right. \\
&\qquad+\sum_{m=0}^{N-1}\{-D\Delta t p_m^2+ip_m[x_{m+1}-2n_mL-(-1)^{n_m}x_m]\} \\
&\qquad+\tfrac{1}{2}\sum_{m=0}^{N-1}\sum_{q=0}^{N-1}\sigma^2\delta(y_{m+1}-y_{q+1})\left[\frac{n_mL}{D}+\frac{[-1+(-1)^{n_m}]x_m}{2D}-ip_m\Delta t\right] \\
&\qquad\left.\times\left[\frac{n_qL}{D}+\frac{[-1+(-1)^{n_q}]x_q}{2D}-ip_q\Delta t\right]\right\}.
\end{aligned} \tag{10}$$

Although this expression contains factors of $(-1)^n$ and i, it is nonetheless real and positive, since it is a probability. Furthermore, given our assumptions about the velocity fluctuations, Eq. (10) is an exact expression. We will use the variational method to approximate the remaining integrals.

III. VARIATIONAL CALCULATION

Suppose we have a path-integral expression for which we cannot do the integrals, $e^{-W}\equiv\int Dxe^{-S}$, where S is broadly analogous to an action. Suppose further that we also have S_A, in some sense an approximation of S, for which we can do the integrals $e^{-W_A}\equiv\int Dxe^{-S_A}$. We will call S_A a "test action." We define the average of a functional F as

$$\langle F\rangle_A\equiv\frac{\int DxFe^{-S_A}}{\int Dxe^{-S_A}}\ . \tag{11}$$

We first rewrite our original path-integral expression

$$\begin{aligned}
e^{-W}&=\frac{\left[\int Dxe^{-S_A}\right]\left[\int Dx\, e^{-(S-S_A)}e^{-S_A}\right]}{\left[\int Dxe^{-S_A}\right]} \\
&\equiv e^{-W_A}\langle e^{-(S-S_A)}\rangle_A\ .
\end{aligned} \tag{12}$$

Then, using a standard convexity inequality, we get

$$\langle e^{-(S-S_A)}\rangle_A\geq e^{-\langle S-S_A\rangle_A} \tag{13}$$

and from Eqs. (12) and (13) it follows that

$$W\leq W_A+\langle S-S_A\rangle_A\equiv W_{\text{eff}}\ . \tag{14}$$

We thus end up with an upper bound for W, or equivalently, a lower bound for e^{-W} [17]. An equation analogous to (14) can be obtained for the momentum representation as well [12]. The bound can be optimized with respect to variations of any free parameters in W_A. For our problem, $e^{-W}=\int dy_N\langle G(\mathbf{r}_N,t_N;\mathbf{r}_0,t_0)\rangle$, with $\langle G(\mathbf{r}_N,t_N;\mathbf{r}_0,t_0)\rangle$ given by (10). We integrate over y_N because we are interested in *when* the particle leaves the interval, but not *where*. The choice of S_A depends on two important considerations, one being whether or not we can do the integrals, and the other being how well the resulting e^{-W_A} fits our expectation of the tracer particle's average behavior. Now, the stratified system has been thoroughly investigated in free space [3,8,10,18]: the first two moments of x are given by $\langle x(t)\rangle=0$ and $\langle x^2(t)\rangle\sim t^\alpha$, with $\alpha=3/2$, and the shape of the distribution itself is known for certain limiting cases. If $x/t^{\alpha/2}$ is small, then

$$\langle e^{-W}\rangle\sim\exp\left[-\beta_1\left[\frac{x}{t^{\alpha/2}}\right]^2\right] \tag{15a}$$

and if $x/t^{\alpha/2}$ is large, then

$$\langle e^{-W}\rangle\sim\exp\left[-\beta_2\left[\frac{x}{t^{\alpha/2}}\right]^{4/3}\right]\ . \tag{15b}$$

Since we require a calculation that can be done analytically, we choose S_A so that e^{-W_A} is a Gaussian distribution. Although this does not agree with the limiting case of Eq. (15b), it does agree with the limiting case of Eq. (15a), so our choice is not only necessary in practice, but reasonable as well. We can easily incorporate our knowledge of the first two moments of x in S_A. Although α is known for the free space problem, we can leave it unspecified in S_A, assuming only that $\alpha\geq 1$. This will allow us to frame the first-passage-time calculation a little more generally. We note that

$$G'(x,t;x_0,t_0)=\frac{1}{[4\pi E(t^\alpha-t_0^\alpha)]^{1/2}}\exp\left\{-\frac{(x-x_0)^2}{4E(t^\alpha-t_0^\alpha)}\right\} \tag{16}$$

satisfies

$$\left[\frac{\partial}{\partial t}-\alpha E t^{\alpha-1}\frac{\partial^2}{\partial x^2}\right]G'(x,t;x_0,t_0)=\delta(x-x_0)\delta(t-t_0) \tag{17}$$

and that

$$G'(x_{N+1},t_{N+1};x_0,t_0)=\int dx_N\frac{1}{[4\pi E(t_{N+1}^\alpha-t_N^\alpha)]^{1/2}}\exp\left\{-\frac{(x_{N+1}-x_N)^2}{4E(t_{N+1}^\alpha-t_N^\alpha)}\right\}G'(x_N,t_N;x_0,t_0) \tag{18}$$

for free space. Therefore, imposing the boundary conditions of the first-passage-time problem at $x=\pm L$, and working from analogy with e^{-W}, we will take

$$e^{-W_A}=\int dy_N\prod_{j=1}^{N-1}\int dx_j dy_j\prod_{k=0}^{N-1}\int\frac{dp_k}{2\pi}\prod_{l=0}^{N-1}\sum_{n_l=-\infty}^{+\infty}(-1)^{n_l}\frac{1}{(4\pi D\Delta t)^{N/2}}\exp\left\{-\sum_{m=0}^{N-1}\frac{(y_{m+1}-y_m)^2}{4D\Delta t}\right\}$$
$$\times\exp\left\{\sum_{m=0}^{N-1}[-E(t_{m+1}^\alpha-t_m^\alpha)p_m^2+ip_m\{x_{m+1}-2n_mL-(-1)^{n_m}x_m\}]\right\}. \tag{19}$$

At this point E and α are undetermined variational parameters. From these definitions, we can see that

$$S-S_A=\sum_{m=0}^{N-1}p_m^2[D\Delta t-E(t_{m+1}^\alpha-t_m^\alpha)]-\tfrac{1}{2}\sum_{m=0}^{N-1}\sum_{q=0}^{N-1}\sigma^2\delta(y_{m+1}-y_{q+1})\left[\frac{n_mL}{D}+\frac{[-1+(-1)^{n_m}]x_m}{2D}-ip_m\Delta t\right]$$
$$\times\left[\frac{n_qL}{D}+\frac{[-1+(-1)^{n_q}]x_q}{2D}-ip_q\Delta t\right]. \tag{20}$$

After some work, we obtain

$$e^{-W_A}=\frac{1}{[4\pi E(t_N^\alpha-t_0^\alpha)]^{1/2}}\sum_{n=-\infty}^{+\infty}(-1)^n\exp\left\{-\frac{[x_N-2nL-(-1)^n x_0]^2}{4E(t_N^\alpha-t_0^\alpha)}\right\} \tag{21}$$

and

$$e^{-W_A}\langle S-S_A\rangle=\frac{[D(t_N-t_0)-E(t_N^\alpha-t_0^\alpha)+4\sigma^2(t_N^{3/2}-t_0^{3/2})/3(4\pi D)^{1/2}]}{2E(t_N^\alpha-t_0^\alpha)[4\pi E(t_N^\alpha-t_0^\alpha)]^{1/2}}$$
$$\times\sum_{n=-\infty}^{+\infty}(-1)^n\exp\left\{-\frac{[x_N-2nL-(-1)^n x_0]^2}{4E(t_N^\alpha-t_0^\alpha)}\right\}\left\{1-\frac{[x_N-2nL-(-1)^n x_0]^2}{2E(t_N^\alpha-t_0^\alpha)}\right\}. \tag{22}$$

We have in Eq. (14) an upper bound for W. We expect the bound to be most reliable at the distribution's point of maximum probability, $x_N=x_0$, as this is where the most representative tracer particles still in the interval would be. Since we have assumed that the particle starts exactly between the two absorbing walls, $x_0=0$. We take $t_0=0$ with no loss of generality, and set $t_N=t$. The appropriate quantities become

$$e^{-W_A}\to\frac{1}{(4\pi E t^\alpha)^{1/2}}\sum_{n=-\infty}^{+\infty}(-1)^n\exp\left\{-\frac{n^2L^2}{Et^\alpha}\right\} \tag{23}$$

and

$$e^{-W_A}\langle S-S_A\rangle\to\left[Dt-Et^\alpha+\frac{4\sigma^2t^{3/2}}{3(4\pi D)^{1/2}}\right]\frac{1}{2Et^\alpha(4\pi Et^\alpha)^{1/2}}\sum_{n=-\infty}^{+\infty}(-1)^n\exp\left\{-\frac{n^2L^2}{Et^\alpha}\right\}\left\{1-\frac{2n^2L^2}{Et^\alpha}\right\}. \tag{24}$$

The values of the free parameters are fixed by setting $(\partial/\partial E)W_{\text{eff}}=0$, which reduces to

$$Et^\alpha=Dt+\frac{4\sigma^2t^{3/2}}{3(4\pi D)^{1/2}}. \tag{25}$$

In other words, the optimum value of $e^{-W_A}\langle S-S_A\rangle$ is zero. In the long-time limit, $Et^{\alpha}\to 4\sigma^2 t^{3/2}/3(4\pi D)^{1/2}$, so $E\to 4\sigma^2/3(4\pi D)^{1/2}$ and $\alpha\to\frac{3}{2}$. It is interesting to note here that a first order perturbation expansion in powers of the fluctuations corresponds to $Et^{\alpha}=Dt$ in Eqs. (23) to (25). Thus the first order perturbative result is itself a lower bound, and not generally the optimal one [11].

Setting as before $x_0=0$, $t_0=0$, $x_N=x$, and $t_N=t$, and integrating over the final vertical position, the variational bound for the average concentration becomes

$$\langle G'(x,t)\rangle=\frac{1}{(4\pi Et^{3/2})^{1/2}}\times\sum_{n=-\infty}^{+\infty}(-1)^n\exp\left\{-\frac{(x-2nL)^2}{4Et^{3/2}}\right\} \tag{26}$$

with E given above. We can obtain a convenient form for the exit time distribution $p(t)=-\partial/\partial t\int_{-L}^{+L}dx\langle G'(x,t)\rangle$ [cf. Eq. (3)] by using the equation of motion for $\langle G'(x,t)\rangle$, Eq. (17):

$$\begin{aligned}p(t)&=\int_{-L}^{+L}dx\left[-\frac{\partial}{\partial t}\langle G'(x,t)\rangle\right]\\&=\int_{-L}^{+L}dx\left[-\alpha Et^{\alpha-1}\frac{\partial^2}{\partial x^2}\langle G'(x,t)\rangle\right].\end{aligned} \tag{27}$$

Note that the exit time distribution is essentially the total current out of the region of interest. We find with a little rewriting that

$$p(t)=\frac{3L}{2t}\frac{1}{(4\pi Et^{3/2})^{1/2}}\times\sum_{n=-\infty}^{+\infty}(-1)^n(1-2n)\exp\left\{-\frac{L^2(1-2n)^2}{4Et^{3/2}}\right\}. \tag{28}$$

We can compute the sum

$$\sum_{n=-\infty}^{+\infty}(-1)^n(1-2n)\exp\left\{-\frac{L^2(1-2n)^2}{4Et^{3/2}}\right\} \tag{29}$$

by approximating it as an integral, then, either by completing the square or by the method of steepest descent. The sum becomes

$$\left[\frac{\pi Et^{3/2}}{L^2}\right]^{3/2}\exp\left\{-\frac{\pi^2Et^{3/2}}{4L^2}\right\}. \tag{30}$$

This result depends on the assumption that $\pi^2Et^{3/2}/8L^2\gg 1$, for if $8L^2/\pi^2Et^{3/2}\gg 1$, we expect the sum would be dominated by its largest term, $n=0$. In this approximation,

$$p(t)\to\frac{\sigma^2t^{1/2}\pi^{1/2}}{D^{1/2}L^2}\exp\left\{-\frac{\sigma^2t^{3/2}\pi^{3/2}}{6L^2D^{1/2}}\right\}. \tag{31}$$

This is not a simple exponential, as occurs in the case of two layers [7]. The mean first passage time

$$\begin{aligned}\langle T\rangle&=\int_0^{+\infty}dt\,tp(t)\\&\to\frac{6^{5/3}D^{1/3}L^{4/3}}{\sigma^{4/3}\pi^2}\int_0^{+\infty}dt\,t^{3/2}\exp\{-t^{3/2}\}\end{aligned} \tag{32}$$

is proportional to $L^{4/3}$, as predicted by the naive argument [13].

IV. SUMMARY

We have used Feynman's variational method to approximate the Green function corresponding to convective-diffusive transport through a layered medium with velocity parallel to the layering and absorbing boundaries normal to the velocity. From this Green function, we have obtained a variational estimate of the exit time distribution and the mean first passage time for a test particle starting between the boundaries. Since $e^{-W}\ge e^{-W_{\rm eff}}$, our method provides a lower bound for the Green function, and thus a lower bound for the mean first passage time [19]. In the limit of large L, our result of $\langle T\rangle\sim L^{4/3}$ is therefore consistent with Redner's result $\langle T\rangle\sim(L\ln L)^{4/3}$ [14]. We expect our exit time distribution will give increasingly unsatisfactory results for higher moments of the first passage time, since our variational bound for the average Green function is Gaussian, while the known tail of the average Green function [Eq. (15b)] has broader wings than a Gaussian, and the wings of a distribution more strongly influence its higher moments.

A very interesting aspect of our variational result for the Green function is that one would get the same result by a direct application of King's partial-summation perturbation approach [16]. As our calculation is somewhat more involved than King's, one could reasonably wonder if the extra trouble is necessary. Perhaps it is not strictly necessary, but it does give us an alternative way of thinking about what we do to get the result. King's method amounts to the summation of a particularly convenient subset of terms of the full perturbation expansion. Feynman's variational method, on the other hand, attempts to find the Gaussian distribution which is a best lower bound to the actual Green function. These two methods give the same result for this problem because motion transverse to the layering is not affected by convection, leaving all the interesting enhanced dispersion to take place in one dimension. The story would be different if convection were not parallel to the layering; the interplay between convection and diffusion would no longer induce long-term correlations in time for fluctuations in the direction of flow, and the overall effective behavior would be normal diffusion with enhanced coefficients both parallel and transverse to the flow [8]. Of course, strictly speaking, the perturbation method is supposed to be limited to situations for which the perturbed state and the averaged state are close in some sense to the unperturbed state. For this problem, then, the perturbation expansion would be expected to fail at large t, even as this is the parameter range of interest.

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APPENDIX

Defining path integrals with position-dependent parameters can be a tricky business. The discussion in our previous paper [12] was somewhat flawed, and we correct matters here. We consider the incompressible CDE with position-dependent velocity and diffusion, defined for simplicity over all space:

$$\left[\frac{\partial}{\partial t}+\mathbf{u}(\mathbf{r})\cdot\nabla-\nabla\cdot\mathbf{D}(\mathbf{r})\cdot\nabla\right]c(\mathbf{r},t)=0 . \tag{A1}$$

Let us suppose for a moment that both the velocity and the dispersion tensor of Eq. (A1) are constant, $\mathbf{u}(\mathbf{r})\rightarrow\mathbf{u}_0$ and $\mathbf{D}(\mathbf{r})\rightarrow\mathbf{D}_0$. Then the Green function $G_0(\mathbf{r}-\mathbf{r}_0,t-t_0)$ for the resulting equation is defined by

$$\left[\frac{\partial}{\partial t}+\mathbf{u}_0\cdot\nabla-\nabla\cdot\mathbf{D}_0\cdot\nabla\right]G_0(\mathbf{r}-\mathbf{r}_0,t-t_0)=\delta(\mathbf{r}-\mathbf{r}_0)\delta(t-t_0) \tag{A2}$$

and is no more than the probability that a tracer particle starting at $(\mathbf{r}_0,t_0)$ will end up at $(\mathbf{r},t)$. This probability is in turn the sum over all possible paths of the probability that the tracer particle will take a particular path from $(\mathbf{r}_0,t_0)$ to $(\mathbf{r},t)$. Equation (A2) has the following path-integral solution [20–22]:

$$G_0(\mathbf{r}_N-\mathbf{r}_0,t_N-t_0)=\int_{\mathbf{r}(t_0)=\mathbf{r}_0}^{\mathbf{r}(t_N)=\mathbf{r}_N} D\mathbf{r}\exp\left\{-\tfrac{1}{4}\int_{t_0}^{t_N}d\tau\left[\frac{d\mathbf{r}}{d\tau}-\mathbf{u}_0\right]\cdot\frac{1}{\mathbf{D}_0}\cdot\left[\frac{d\mathbf{r}}{d\tau}-\mathbf{u}_0\right]\right\} . \tag{A3}$$

It is useful to see how (A3) is obtained. Suppose we wish to know the probability that a tracer particle will follow a given path $\mathbf{r}(t)$ from $(\mathbf{r}_0,t_0)$ to $(\mathbf{r}_N,t_N)$. We divide the time interval into N equal segments, of length $\Delta t\equiv(t_N-t_0)/N$, and approximate the path by $N+1$ points $(\mathbf{r}_k\equiv\mathbf{r}(t_k),\ t_k\equiv t_0+k\Delta t)$, where $0\le k\le N$. The probability $\rho(k-1,k)$ of going from $(\mathbf{r}_{k-1},t_{k-1})$ to $(\mathbf{r}_k,t_k)$ can be obtained from (A2):

$$\rho(k-1,k)=\frac{1}{[4\pi\Delta t]^{3/2}[\det\mathbf{D}_0]^{1/2}}\exp\left\{-\frac{\Delta t}{4}\left[\frac{\mathbf{r}_k-\mathbf{r}_{k-1}}{\Delta t}-\mathbf{u}_0\right]\cdot\frac{1}{\mathbf{D}_0}\cdot\left[\frac{\mathbf{r}_k-\mathbf{r}_{k-1}}{\Delta t}-\mathbf{u}_0\right]\right\} \tag{A4}$$

and the probability for taking the entire path is $\prod_{k=1}^{N}\rho(k-1,k)$. To get the Green function, we integrate this over all intermediate positions:

$$G_0(\mathbf{r}_N-\mathbf{r}_0,t_N-t_0)=\int d\mathbf{r}_1\cdots\int d\mathbf{r}_{N-1}\frac{1}{(4\pi\Delta t)^{3N/2}[\det\mathbf{D}_0]^{N/2}}\times\exp\left\{-\frac{\Delta t}{4}\sum_{k=1}^{N}\left[\frac{\mathbf{r}_k-\mathbf{r}_{k-1}}{\Delta t}-\mathbf{u}_0\right]\cdot\frac{1}{\mathbf{D}_0}\cdot\left[\frac{\mathbf{r}_k-\mathbf{r}_{k-1}}{\Delta t}-\mathbf{u}_0\right]\right\} . \tag{A5}$$

This is the proper way to interpret (A3). We can easily show that the Green function of Eq. (A5) obeys (A2) to first order in Δt, assuming only that the irregularity is relatively well behaved [21]. For simplicity let us set $\mathbf{r}_0\equiv 0$ and $t_0\equiv 0$. Then $G_0(\mathbf{r}_{N+1},t_{N+1})$ can clearly be written as

$$G_0(\mathbf{r}_{N+1},t_{N+1})=\int d\mathbf{r}_N\frac{1}{(4\pi\Delta t)^{3/2}(\det\mathbf{D}_0)^{1/2}}\times\exp\left\{-\frac{\Delta t}{4}\left[\frac{\mathbf{r}_{N+1}-\mathbf{r}_N}{\Delta t}-\mathbf{u}_0\right]\cdot\frac{1}{\mathbf{D}_0}\cdot\left[\frac{\mathbf{r}_{N+1}-\mathbf{r}_N}{\Delta t}-\mathbf{u}_0\right]\right\}G(\mathbf{r}_N,t_N) . \tag{A6}$$

Now we set $\mathbf{r}_{N+1}\equiv\mathbf{r}$, $\mathbf{r}_{N+1}-\mathbf{r}_N\equiv y$, $t_N\equiv t$. With these, (A6) can be rewritten

$$G_0(\mathbf{r},t+\Delta t)=\int d\mathbf{y}\frac{1}{(4\pi\Delta t)^{3/2}(\det\mathbf{D}_0)^{1/2}}\exp\left\{-\frac{\Delta t}{4}\left[\frac{\mathbf{y}}{\Delta t}-\mathbf{u}_0\right]\cdot\frac{1}{\mathbf{D}_0}\cdot\left[\frac{\mathbf{y}}{\Delta t}-\mathbf{u}_0\right]\right\}G(\mathbf{r}-\mathbf{y},t) . \tag{A7}$$

If the irregularity of the motion is relatively well behaved, then $\mathbf{y}$ will be small, and $\mathbf{G}_0(\mathbf{r}-\mathbf{y},t)$ can be expanded in a Taylor series around $\mathbf{y}=0$. Likewise $G_0(\mathbf{r},t+\Delta t)$ can be expanded in a Taylor series around $\Delta t=0$. Performing all necessary computations, (A7) becomes

$$G_0(\mathbf{r},t)+\Delta t\frac{\partial}{\partial t}G_0(\mathbf{r},t)+O((\Delta t)^2)=G_0(\mathbf{r},t)-\Delta t\mathbf{u}_0\cdot\nabla G_0(\mathbf{r},t)+\Delta t\nabla\cdot\mathbf{D}_0\cdot\nabla G_0(\mathbf{r},t)+O((\Delta t)^2) , \tag{A8}$$

from which it follows that the Green function of Eq. (A5) obeys Eq. (A2) to first order in Δt.

Things become a bit more complicated if we wish to allow for space-dependent velocities and dispersion tensors. The

Green function for Eq. (A1), $G(\mathbf{r},\mathbf{r}_0,t-t_0)$ is defined by

$$\left[\frac{\partial}{\partial t}+\mathbf{u}(\mathbf{r})\cdot\nabla-\nabla\cdot\mathbf{D}(\mathbf{r})\cdot\nabla\right]G(\mathbf{r},\mathbf{r}_0 t-t_0)=\delta(\mathbf{r}-\mathbf{r}_0)\delta(t-t_0)\ . \tag{A9}$$

We cannot simply go by analogy with the constant-parameter case, and suppose the solution to be

$$G(\mathbf{r}_N,\mathbf{r}_0,t_N-t_0)=\int_{\mathbf{r}(t_0)=\mathbf{r}_0}^{\mathbf{r}(t_N)=\mathbf{r}_N}D\mathbf{r}\exp\left\{-\tfrac{1}{4}\int_{t_0}^{t_N}d\tau\left[\frac{d\mathbf{r}}{d\tau}-\mathbf{u}(\mathbf{r})\right]\cdot\frac{1}{\mathbf{D}(\mathbf{r})}\cdot\left[\frac{d\mathbf{r}}{d\tau}-\mathbf{u}(\mathbf{r})\right]\right\} \tag{A10}$$

because using the method just above, (A10) can be shown to obey

$$\frac{\partial}{\partial t}G(\mathbf{r},\mathbf{r}_0,t-t_0)+\mathbf{u}(\mathbf{r})\cdot\nabla G(\mathbf{r},\mathbf{r}_0,t-t_0)=D_i(\mathbf{r})\frac{\partial^2}{\partial r_i^2}G(\mathbf{r},\mathbf{r}_0,t-t_0) \tag{A11}$$

to first order in Δt. But

$$\frac{\partial}{\partial r_i}\left[D_i(\mathbf{r})\frac{\partial}{\partial r_i}G\right]=\left[\frac{\partial}{\partial r_i}D_i(\mathbf{r})\right]\frac{\partial G}{\partial r_i}+D_i(\mathbf{r})\frac{\partial^2 G}{\partial r_i^2}\quad\text{(no sum)} \tag{A12}$$

suggests that

$$G(\mathbf{r}_N,\mathbf{r}_0,t_N-t_0)=\int_{\mathbf{r}(t_0)=\mathbf{r}_0}^{\mathbf{r}(t_N)=\mathbf{r}_N}D\mathbf{r}\exp\left\{-\tfrac{1}{4}\int_{t_0}^{t_N}d\tau\left[\frac{d\mathbf{r}}{d\tau}-\mathbf{u}(\mathbf{r})+\mathbf{v}(\mathbf{r})\right]\cdot\frac{1}{\mathbf{D}(\mathbf{r})}\cdot\left[\frac{d\mathbf{r}}{d\tau}-\mathbf{u}(\mathbf{r})+\mathbf{v}(\mathbf{r})\right]\right\}, \tag{A13}$$

where

$$v_i(\mathbf{r})\equiv\frac{\partial}{\partial r_i}D_i(\mathbf{r})\quad\text{(no sum)} \tag{A14}$$

will obey (A9). We can show this to be so, using the method outlined above. The proper way to interpret (A13) would then be

$$G(\mathbf{r}_N,\mathbf{r}_0,t_N-t_0)=\int d\mathbf{r}_1\cdots\int d\mathbf{r}_{N-1}\frac{1}{(4\pi\Delta t)^{3/2}[\det\mathbf{D}(\mathbf{r}_1)]^{1/2}}\cdots\frac{1}{(4\pi\Delta t)^{3/2}[\det\mathbf{D}(\mathbf{r}_N)]^{1/2}}$$
$$\times\exp\left\{-\frac{\Delta t}{4}\sum_{k=1}^{N}\left[\frac{\mathbf{r}_k-\mathbf{r}_{k-1}}{\Delta t}-\mathbf{u}(\mathbf{r}_k)+\mathbf{v}(\mathbf{r}_k)\right]\cdot\frac{1}{\mathbf{D}(\mathbf{r}_k)}\cdot\left[\frac{\mathbf{r}_k-\mathbf{r}_{k-1}}{\Delta t}-\mathbf{u}(\mathbf{r}_k)+\mathbf{v}(\mathbf{r}_k)\right]\right\}. \tag{A15}$$

We use $(\mathbf{r}_k-\mathbf{r}_{k-1})/\Delta t$ in Eq. (A15) for the velocity of the particle as it moves from $\mathbf{r}_{k-1}$ to $\mathbf{r}_k$; although this is the natural and obvious choice to make, it is not the only possible choice. Other choices differ from ours by terms of order Δt, and change the observations which follow. For cases of varying $\mathbf{D}(\mathbf{r})$ and $\mathbf{u}(\mathbf{r})$, our selection of $\mathbf{D}(\mathbf{r}_k)$ and $\mathbf{u}(\mathbf{r}_k)$ for their values respectively as the particle moves from $\mathbf{r}_{k-1}$ to $\mathbf{r}_k$ is most convenient. With a minor change in the drift velocity, we obtain a path-integral expression which obeys the proper equation of motion, as shown above. Other selections for $\mathbf{D}(\mathbf{r})$, such as $\mathbf{D}(\mathbf{r}_{k-1})$, $\mathbf{D}(\frac{1}{2}[\mathbf{r}_{k-1}+\mathbf{r}_k])$, or $\frac{1}{2}[\mathbf{D}(\mathbf{r}_k)+\mathbf{D}(\mathbf{r}_{k-1})]$, define path-integral expressions which do not obey the proper equation of motion, and which cannot be made to do so by a simple redefinition of the drift velocity. A similar observation can be made about other selections for $\mathbf{u}(\mathbf{r})$.

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[13] For this problem, we know that $\langle x^2(t)\rangle \sim t^{3/2}$. Naively, we might think that this would imply $L^2 \sim \langle T\rangle^{3/2}$, from which we get $\langle T\rangle \sim L^{4/3}$. This sort of handwaving argument is, of course, not always correct.

[14] S. Redner (private communication).

[15] The Rayleigh-Ritz technique familiar from standard quantum mechanics may be a suitable starting place, but some differences, as between what is calculated in quantum mechanics (a complex probability density) and what is calculated here (a real first passage time), make the application problematic. We are now investigating application of the Rayleigh-Ritz method to this problem.

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[19] From $e^{-W} \geq e^{-W_{\rm eff}}$ it follows that $\int_{-L}^{+L} dx\, e^{-W} \geq \int_{-L}^{+L} dx\, e^{-W_{\rm eff}}$, i.e., we have a lower bound for the probability that a tracer particle is still within the interval. Since $\langle T\rangle = \int_0^\infty dt\, t(-1)(\partial/\partial t)\int_{-L}^{+L} dx\, e^{-W} = \int_0^\infty dt \int_{-L}^{+L} dx\, e^{-W}$, our estimate of $\langle T\rangle$ is a lower bound for the exact value.

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