Journal of Statistical Physics, Vol. 85, Nos. 1/2, 1996

# Asymptotic Results for a Persistent Diffusion Model of Taylor Dispersion of Particles

**Gerardo Soto-Campos**[1] **and Robert M. Mazo**[1]

*Received April 26, 1994; final March 6, 1996*

We study Taylor diffusion for the case when the diffusion transverse to the bulk motion is a persistent random walk on a one-dimensional lattice. This is mapped onto a Markovian walk where each lattice site has two internal states. For such a model we find the effective diffusion coefficient which depends on the rate of transition among internal states of the lattice. The Markovian limit is recovered in the limit of infinite rate of transitions among internal states; the initial conditions have no role in the leading-order time-dependent term of the effective dispersion, but a strong effect on the constant term. We derive a continuum limit of the problem presented and study the asymptotic behavior of such limit.

**KEY WORDS:** Taylor diffusion; non-Markovian processes; composite stochastic processes.

## 1. INTRODUCTION

In this paper we study a case of what has been called composite stochastic processes.[1] A physical example of such a process is Taylor dispersion.[2] In this example, the dispersion in position of a particle suspended in a fluid that is undergoing laminar flow through a cylinder is enhanced by the radial motion of the particle, which changes by a diffusion process. Chromatography is another examples.[3]

Van den Broeck and Mazo[4] have studied a closely related model. One has particles moving parallel to the $x$ axis, as above. The $y$ axis, however, is divided into strata; an equivalent description is that the $y$ axis is a one-dimensional lattice. The particles make a random walk among the

[1] Chemistry Department and Institute of Theoretical Science, University of Oregon, Eugene, Oregon 97403-1229.



0022-4715/96/1000-0165$09.50/0 

strata (lattice sites) while undergoing convection in the $x$ direction. The convective velocity of a particle at any given time thus becomes a random variable.

The random walk between the strata was treated as a Pearson walk between nearest neighbor strata. In this paper, we study the same general problem for the case when the random walk is persistent.[5-7] A persistent walk in one dimension is a random walk in which the probability of moving to the right or to the left in the $n$th step depends on the *direction* of the move taken at step $n-1$.

The physical interest of this problem is to see if the persistence of the walk has any effect on the longitudinal (i.e., $x$ direction) dispersion of the particle positions about their mean. Taylor dispersion is a common method of measuring diffusion coefficients in fluids, so it is important to investigate all facets of the connection between the measured dispersion and the molecular diffusion coefficient.

In Taylor dispersion, the dispersion of the $x$ position of particles about their mean varies linearly with time, $\langle(\delta x)^2\rangle \sim t$, for long times. Here, long times means those longer than necessary for the convecting particle to sample the entire transverse ($y$ direction) velocity field. Thus the fact that the system is bounded in the $y$ direction is essential, as well as corresponding to many experimental conditions. Variants of the dispersion problem in which the $y$ direction is unbounded have been studied, and the results are quite different from those of Taylor.

In particular, Matheron and de Marsily[8] have considered the case of a layered medium where the velocities in each layer are random variables, but the walk between layers is Markovian; they started from the conventional convective-diffusion equation. They were interested in a system of large transverse width, and time short according to the definition above. Hence they made the approximation that the medium was unbounded. Some aspects of this problem were also treated by Mazo and Van den Broeck.[9] In this problem, the dispersion varies as $t^{3/2}$. Similar results were found by Gaveau and Shulman.[10] Ben-Naim *et al.*[11] considered the problem in which the longitudinal velocity varied as $y^\beta$ and found a longitudinal dispersion varying as $t^{2+\beta}$. This work is also based on the conventional convective diffusion equation and assumed an unbounded medium.

It is not at all surprising that the long-time bounded-medium result does not show up in these works. In an infinite medium a particle never has time to sample the entire distribution of longitudinal velocities. A similar difference between a finite and an infinite system shows up in the related problem of spin depolarization[12,13] by random walk. All our results are for the case of a finite system with reflecting boundary conditions.

## 2. THE MODEL AND ITS EQUATIONS OF MOTION

The persistent random walk we use in this article is that treated in the model of Kac,[7] with the addition of a convective term. The model is slightly different from that of Goldstein,[6] reviewed by Weiss and Rubin.[4] A random walk with persistence is non-Markovian. We treat it by the known technique of embedding it in a higher dimensional Markov process, i.e., a Markov random walk in which the walker has internal states, which we label by the symbols + and −. The walk is on an $N$-site lattice in continuous time.

Denote the probability that the walker is on lattice site $j$ at longitudinal position $x$ at time $t$ while in internal state $\alpha$, by $P_j(\alpha, x, t)$. Here $\alpha = +$ is to be interpreted as the step leading to the walker's presence at site $j$ originating at site $j-1$; $\alpha = -$ indicates that the origin of the previous step was $j+1$. Transitions such as $(j, +) \to (j+1, -)$ are not allowed in this model. The transition rate for $j \to j+1$ in time $dt$ is denoted by $k_j\, dt + o(dt)$; the rate for $j \to j-1$ in $dt$ is $l_j\, dt + o(dt)$.

Particles do not retain their internal state indefinitely. We assume that the memory of the direction of the last step decays in time, so that the probability of the transitions $(j, +) \to (j, -)$ and $(j, -) \to (j, +)$ in time $dt$ is $r\, dt + o(dt)$. The rate $r$ is a kind of inverse lifetime of the internal state. $u_j$ is the longitudinal velocity of a particle in stratum $j$.

Applying the usual balance-of-probability arguments (change equals gain minus loss) to the states $(j, +)$ and $(j, -)$, one obtains easily

$$P_j(+, x + u_j\, dt, t + dt) = k_{j-1}\, dt P_{j-1}(+, x, t) + r\, dt P_j(-, x, t) \\ + (1 - (k_j + r)\, dt)\, P_j(+, x, t) \tag{1}$$

and a similar equation for $P_j(-, x + u_j\, dt, t + dt)$. The quantity of interest to us is the total probability of being in state $j$,

$$P_j(x, t) = P_j(+, x, t) + P_j(-, x, t) \tag{2a}$$

For reasons of symmetry we introduce the quantity

$$G_j(x, t) = P_j(+, x, t) - P_j(-, x, t) \tag{2b}$$

for the second dependent variable at site $j$. Equations (2) can be expressed in terms of $P_j$ and $G_j$ as (written in matrix form for convenience)

$$\partial_t P(x, t) = -\mathbf{U}\, \partial_x P(x, t) + \mathbf{K} P(x, t) + \mathbf{L} G(x, t) \tag{3}$$

$$\partial_t G(x, t) = -\mathbf{U}\, \partial_x G(x, t) + \mathbf{L} P(x, t) - 2r\mathbf{1} G(x, t) + \mathbf{K} G(x, t) \tag{4}$$

Here $P = \mathrm{col}(P_1, ..., P_N)$, $G = \mathrm{col}(G_1, ..., G_N)$, $\mathbf{U} = \mathrm{diag}(U_1, ..., U_N)$, and

$$K_{j,m} = \tfrac{1}{2}[k_{j-1}\,\delta_{j-1,m} + l_{j+1}\delta_{j+1,m} - (k_j + l_j)\,\delta_{j,m}]$$
$$L_{j,m} = \tfrac{1}{2}[k_{j-1}\delta_{j-1,m} - l_{j+1}\delta_{j+1,m} - (k_j - l_j)\,\delta_{j,m}]$$

The moments, in particular the first and the second moments of $P$, are the quantities most closely related to experiments. It is easy to eliminate $G$ between Eqs. (3) and (4) when $\mathbf{U} = 0$, i.e., in the case of no convection. However, since the matrices $\mathbf{K}$ and $\mathbf{U}$ do not commute, we have not been able to eliminate $G$ from the pair (3), (4). Consequently, in evaluating the moments of $P$ we must use both members of the pair.

## 3. MOMENTS OF THE DISTRIBUTION, *P*

It is useful to introduce a barycentric coordinate system traveling with the mean velocity of the flow $\bar{u} = \sum_{m=1}^{N} u_m P_m^{\mathrm{st}}$, where $P_i^{\mathrm{st}}$ is the asymptotic, steady-state value of $P_i(x, t)$ as $t \to \infty$. The barycentric longitudinal coordinate is $\xi = x - \bar{u}t$. It is also useful to Laplace transform the resulting differential equations; Laplace transforms are denoted by superior tildes, and $z$ is the Laplace variable.

The resulting equations of motion in Laplace space are, in matrix notation,

$$z\tilde{P}(\xi, z) - P(\xi, t=0) = -(\mathbf{U} - \bar{\mathbf{U}})\,\partial_\xi \tilde{P}(\xi, z) + \mathbf{K}\tilde{P}(\xi, z) + \mathbf{L}\tilde{G}(\xi, z) \quad (5a)$$

$$z\tilde{G}(\xi, z) - G(\xi, t=0) = -(\mathbf{U} - \bar{\mathbf{U}})\,\partial_\xi \tilde{G}(\xi, z) + \mathbf{L}\tilde{P}(\xi, z) - 2r\mathbf{1}\tilde{G}(\xi, z) + \mathbf{K}\tilde{G}(\xi, z) \quad (5b)$$

The probability that a particle is at position $\xi$ regardless of which stratum it resides in is

$$P(\xi, t) = \sum_{j=1}^{N} P_j(\xi, t) \quad (6)$$

$G(\xi, t)$ is defined similarly, and $\tilde{P}$ and $\tilde{G}$ are their Laplace transforms. Now let us define the "moments" by

$$J_p(z) \equiv \int \xi^p \tilde{P}(\xi, z)\, d\xi \quad (7a)$$

$$I_p(z) \equiv \int \xi^p \tilde{G}(\xi, z)\, d\xi \quad (7b)$$

The word "moments" has been written in quotation marks because $G(\xi, t)$ *is not* a probability distribution. [Strictly speaking, neither is $\tilde{P}(\xi, z)$; it is the Laplace transform of a probability distribution.] Indeed, $G(\xi, t)$ need not be positive. Nevertheless, for the sake of brevity, we shall refer to the quantities (7a) and (7b) as moments. $J_p$ and $I_p$ satisfy the equations

$$J_p = p(z-\mathbf{K})^{-1}(\mathbf{U}-\bar{\mathbf{U}})\,J_{p-1} + (z-\mathbf{K})^{-1}\,\mathbf{L}I_p + (z-\mathbf{K})^{-1}\,J_{p,0} \tag{8a}$$

$$I_p = p(z+2r-\mathbf{K})^{-1}(\mathbf{U}-\bar{\mathbf{U}})\,I_{p-1} + (z+2r-\mathbf{K})^{-1}\,\mathbf{L}J_p + (z+2r-\mathbf{K})^{-1}\,I_{p,0} \tag{8b}$$

Here $J_{p,0} = \int \xi^p P(\xi, t=0)\,d\xi$, and similarly for $I_{p,0}$. The central moments of the distribution $P$ are given by

$$\langle(\delta\xi)^p\rangle = \sum_{m=1}^{N} (J_p)_m \tag{9}$$

where $\delta\xi = \xi - \langle\xi\rangle$. These central moments depend, in general, on the initial conditions embedded in $J_{p,0}$ and $I_{p,0}$. We compute here the first and second moments for arbitrary initial conditions.

Let $\{X^\alpha\}$ be the set of right eigenvectors of the matrix $\mathbf{K}$. We assume explicitly that $\mathbf{K}$ is semisimple, i.e., that the set $\{X^\alpha\}$ is complete. This is certainly the case if $\mathbf{K}$ has no repeated eigenvalues. Then we take the initial conditions

$$P(\xi, t=0) = \delta(\xi)\sum_{\alpha=0}^{N-1} c_\alpha X^\alpha \tag{10a}$$

$$G(\xi, t=0) = \delta(\xi)\sum_{\alpha=0}^{N-1} a_\alpha X^\alpha \tag{10b}$$

From Eqs. (8), for $p=1$ one finds $\langle\delta\xi\rangle = 0$ or $\langle\delta x\rangle = \bar{u}t$. This result is precisely what one would expect. For $p=2$, Eqs. (8) and (9) yield

$$\langle(\delta\xi)^2\rangle = -\frac{2}{z}\sum_{l=1}^{N}(u_l-\bar{u})(J_1)_l \tag{11}$$

From Eqs. (8) and considerable algebra, one finds that the leading terms in $\langle(\delta\xi)^2\rangle$ are

$$\langle\delta\xi)^2\rangle = \frac{2}{z^2}\left[\sum_{lmn}(1-\Gamma^{sp}L\Gamma_r L)^{-1}_{lm}\Gamma^{sp}_{mn}(u_n-\bar{u})\,P^{\mathrm{st}}_n + \sum_{lmnqst}(u_l-\bar{u})(1-\Gamma^{sp}L\Gamma_r L)^{-1}_{lm}\,\Gamma^{sp}_{m,n}L_{nq}(\Gamma_r)_{q,s}\,L_{st}P^{\mathrm{st}}_t\right] \tag{12}$$

The development of this equation and many algebraic details of other derivations in this paper can be found in the dissertation of one of the authors.[15] The notation $\Gamma^{sp}$ in Eq. (12) is the modified Green's function, $\Gamma^{sp}(z) \equiv (z-\mathbf{K})^{-1} - |X^0\rangle\langle Y^0|/z$ where $X^\alpha$ and $Y^\alpha$ are the right and left eigenvectors of the matrix $\mathbf{K}$ corresponding to eigenvalue $\lambda_\alpha$ (sp stands for "special"). The other Green's function is $\Gamma_r(z) \equiv (z+2r-\mathbf{K})^{-1}$. First note that Eq. (12) is independent of the coefficients $c_\alpha$ and $a_\alpha$ of Eqs. (10). That is, the leading-order term is independent of initial conditions. For the Markovian case ($r \to \infty$) Van den Broeck and Mazo[4] found an algebraic technique which gives $\langle(\delta x)^2\rangle$ in terms of the transition rates $\{k_j\}$ and $\{l_j\}$ and the fluid profile $u_j$; the advantage of this technique is that one does not need to construct the Green's functions $\Gamma^{sp}$ and $\Gamma_r$ explicitly. However, for the more general (non-Markovian) case of Eq. (12), we do not have an extension of the method of ref. 4. That is because of the appearance of the inverse operator $(1-\Gamma^{sp}L\Gamma_r L)^{-1}_{lm}$, which is difficult to handle algebraically.

The next problem to consider is the next-to-leading order term. We have only treated this problem for the special case $r=\infty$, i.e., the Markovian case. With more algebraic effort the persistent case can be treated by the same method.

One can find from Eq. (11) the following general functional dependence:

$$\langle(\delta x)^2\rangle = 2D_{\text{eff}}t + B + o(1) \tag{13}$$

Van den Broeck and Mazo[4] found the coefficient of the first term, $D_{\text{eff}}$. The second term (in Laplace space) has the form

$$\begin{aligned}
&\langle(\delta\xi)^2\rangle_{z^{-1}\,\text{contribution}}\\
&\quad = \frac{2}{z}\sum_{i,j=1}^{N}(u_i-\bar{u})\,P_i^{\text{st}}\sum_{\alpha\neq 0}\frac{Y_i^\alpha Y_j^\alpha}{\lambda_\alpha^2}(u_j-\bar{u})\,P_j^{\text{st}}\\
&\qquad +\frac{2}{z}\sum_{\alpha\neq 0}\sum_{\beta\neq 0}\sum_{i,j=1}^{N}(u_i-\bar{u})\,P_i^{\text{st}}\frac{Y_i^\beta Y_j^\beta}{\lambda_\beta}(u_j-\bar{u})\,P_j^{\text{st}}c^\alpha\frac{X_j^\alpha}{\lambda_\alpha}
\end{aligned} \tag{14}$$

We have generalized the method that Van den Broeck and Mazo[4] used to evaluate $D_{\text{eff}}$ to compute $B$ directly in terms of the rate coefficients $\{k_j\}$ and $\{l_j\}$ without the necessity of solving the eigenvalue problem for the matrix $\mathbf{K}$. In particular the first term of Eq. (14) (independent of initial conditions) is

$$\frac{2}{z}\sum_{q=1}^{N}(u_q-\bar{u})\,P_q^{\mathrm{st}}\left[-\sum_{s=1}^{N}P_s^{\mathrm{st}}\sum_{i=1}^{s-1}\left(\frac{1}{k_iP_i^{\mathrm{st}}}\right)\sum_{r=1}^{i}P_r^{\mathrm{st}}h_r\right.$$
$$\left.+\sum_{i=1}^{q-1}\left(\frac{1}{k_iP_i^{\mathrm{st}}}\right)\sum_{r=1}^{i}P_r^{\mathrm{st}}h_r\right] \tag{15}$$

where $h_r$ is given by

$$h_r=-\sum_{r=1}^{N}\sum_{l=1}^{r-1}\left(\frac{P_r^{\mathrm{st}}}{k_lP_l^{\mathrm{st}}}\right)(u_m-\bar{u})\,P_m^{\mathrm{st}}$$
$$+\sum_{l=1}^{r-1}\left(\frac{1}{k_lP_l^{\mathrm{st}}}\right)\sum_{m=1}^{l}(u_m-\bar{u})\,P_m^{\mathrm{st}}$$

The derivation of this result can be found in ref. 15. A similar, but much more elaborate procedure gives the second term of Eq. (14) as a function of transition rates and the fluid profile. We do not show it here to save space; it requires using the procedure of ref. 4 two times.[16]

## 4. THE CONTINUUM LIMIT

Taylor dispersion is mostly, though not exclusively, studied in flowing fluids, i.e., in the continuum limit. The results for stratified media go over into the classical results of Taylor[2] and Aris[18] when the number of layers approaches infinity, the width of each layer approaches zero, and the transition rates are scaled to give a reasonable limit.[4] In this section, we study the corresponding continuum limit for the case of the persistent walk.

Here we shall only consider the case when all the $k_j$ are the same, $k$, and all the $l_j$ are the same, $l$, the homogeneous case. The general case presents no new questions of principle. We introduce the layer thickness $\eta$ and the length $y=j\eta$.

In the continuum limit, probabilities must be replaced by probability densities, so we define

$$p(x,y,t)=\frac{(P(x,j;t)}{\eta} \tag{16}$$

and similarly $g(x,y,t)=G(x,j;t)/\eta$. Now take the limit $N\to\infty$, $k$, $l\to\infty$, $\eta\to 0$ in such a way that the products $N_\eta=L$, $k\eta=v$, and $l\eta=w$ remain finite. The discrete variable $j$ goes into the continuous variable $y$, $0\leqslant y\leqslant L$. The stratified velocity becomes the continuous velocity field $u(y)$. In this limit Eqs. (3) and (4) go over into

$$\partial_t p(x, y, t) = -\frac{v-w}{2}\partial_y p(x, y, t) - \frac{v+w}{2}\partial_y g(x, y, t) - u(y)\,\partial_x p(x, y, t) \tag{17a}$$

$$\partial_t g(x, y, t) = -\frac{v+w}{2}\partial_y p(x, y, t) - \frac{v-w}{2}\partial_y g(x, y, t) - 2rg(x, y, t) - u(y)\,\partial_x g(x, y, t) \tag{17b}$$

We shall treat here only the case without bias, $v = w$. We wish to determine the (approximate) equation for $p(x, y; t)$ *averaged* over the transverse ($y$) direction. This quantity

$$n(x, t) \equiv \int_0^L p(x, y, t)\,dy \tag{18}$$

does not obey, rigorously, a closed equation of motion. However, on a long time scale it does obey an approximate closed equation. The situation is similar to that in ordinary Taylor diffusion. In the latter case, the approximate equation is just the diffusion equation with an effective diffusion coefficient $D_{\text{eff}}$.

The problem is to eliminate the fast variables. The only slow variable in the problem is $n(x, t)$, Eq. (18). we assume that, after some induction time, the time dependence of $p(x, y; t)$ and $g(x, y; t)$ comes from the time dependence of $n(x, t)$, the slow variable. More specifically, we assume that, after the induction period, $p$ and $g$ become functionals of $n(x, t)$,

$$p(x, y, t) = p(x, y \mid n(\cdot, t)) \tag{19}$$

and similarly for $g(x, y; t)$. This is the same as Bogoliubov's hypothesis[17] in the kinetic theory of gases.

It is convenient to introduce dimensionless variables $\theta = (v/l)\,t$, $\zeta = x/L$, and $\rho = y/L$. Equations (17) become

$$\partial_\theta p(\zeta, \rho, \theta) = -\mu f(\rho)\,\partial_\zeta p(\zeta, \rho, \theta) - \partial_\rho g(\zeta, \rho, \theta) \tag{20a}$$

$$\partial_\theta g(\zeta, \rho, \theta) = -\mu f(\rho)\,\partial_\zeta g(\zeta, \rho, \theta) - \partial_\rho p(\zeta, \rho, \theta) - (2rL/v)\,g(\zeta, \rho, \theta) \tag{20b}$$

where we have written $u(\rho) = \bar{u} f(\rho)$ and the parameter $\mu$ is defined by $\mu \equiv \bar{u}/v$. Here $\bar{u}$ is the mean speed of the convective flow and $f(\rho)$ describes the shape of the flow profile.

It can be seen from Eq. (20a) that $g$ is the transverse component of the probability current. Consequently we have the boundary conditions

$g(\rho)=0$ at $\rho=0$ and $\rho=1$, and $\partial_\rho p(\rho)=0$ at $\rho=0$ and 1. The condition on $g$ follows from the assumption that the boundary is reflecting; that on $p$ follows from Eq. (20b).

Let us expand the functions $p$ and $g$ in powers of the small parameter $\mu$,

$$p=p^0+\mu p^1+\mu^2 p^2+\cdots \tag{21}$$

and similarly for $g$. The coefficients $p^i$ and $g^i$ may contain additional $\mu$ dependence. It then follows that, to order $\mu^2$, $n$ satisfies

$$\partial_\theta n(\zeta,\theta)=-\mu\int_0^1 d\rho\, f(\rho)\,\partial_\zeta p^0-\mu^2\int_0^1 d\rho\, f(\rho)\,\partial_\zeta p^1 \tag{22}$$

$p^0$ and $p^1$ can be computed explicitly as shown in the Appendix, in a way similar to that familiar from the kinetic theory of gases. Reverting to the original dimensional variables, one gets

$$\begin{aligned}\partial_t n(x,t)= &-\bar{u}\,\partial_x n(x,t)-\frac{\bar{u}^2}{L}\left(\frac{2r}{v^2}\right)\int_0^L dy[f(y)-\bar{f}]\\ &\times\left\{\int_0^{y} dy'\int_0^{y'} dz\,[f(z)-\bar{f}]\right\}\partial_{xx}n(x,t)\end{aligned} \tag{23}$$

where $\bar{f}$ is defined as $\bar{f}=(1/L)\int_0^L dy\, f(y)$.

The coefficient of the term $\partial_{xx}n(x,t)$ in Eq. (23) is the effective diffusion coefficient. By changing the order of integration, it can be written as

$$D_{\text{non-Markov}}=\frac{\bar{u}^2}{L}\left(\frac{2r}{v^2}\right)\int_0^L dy\left\{\int_0^{y} dz[f(z)-\bar{f}]\right\}^2 \tag{24}$$

which is manifestly positive. The effective diffusion coefficient for the classical Taylor case, $D_{\text{Markov}}$, is recovered in the limit $v, r\to\infty$ in such a way that the ratio $v^2/(2r)\equiv D_{\text{mol}}$ remains finite. $D_{\text{mol}}$ is interpreted as the molecular diffusion coefficient.

Thus we see that even when diffusion in the direction transverse to the flow is persistent, the motion in the longitudinal direction still obeys a convective diffusion equation of precisely the same form as when the transverse diffusion is Fickian.

We now have two expressions for the effective diffusion coefficient. For the continuous case we have Eq. (24), while in the stratified, discrete case we have Eq. (12). The continuous transport equation was derived from the discrete one by a limiting process, and the effective diffusion coefficient arose naturally in that process. Nevertheless, it would be worthwhile to see directly how Eq. (12) reduces to Eq. (24) in the continuum limit.

In order to see this we need the explicit form of the Green's function $(\mathbf{K}-\mathbf{L}\Gamma_r\mathbf{L})^{-1}$ in the continuum limit. The notation is a bit misleading since $(\mathbf{K}-\mathbf{L}\Gamma_r\mathbf{L})$ has a zero eigenvalue and hence no inverse. What we mean is the modified Green's function, the inverse on the subspace left when the zero eigenspace is projected out. One finds that this function satisfies a simple second-order differential equation, the solution of which must be used when the sum in (12) is turned into an integral. The details of the calculation can be found in ref. 15, and (24) is the result.

## 5. DISCUSSION AND CONCLUSIONS

Taylor dispersion is the enhancement of diffusion parallel to a flow caused by diffusion transverse to the flow. In the case when the system is stratified transverse to the flow, the transverse diffusion is modeled as a random walk, usually an ordinary Pearson walk. In this paper we have investigated the case where the transverse walk is a persistent walk, perhaps the simplest non-Markovian walk.

The main conclusion to be drawn from this work is that replacing the Pearson walk by a persistent walk makes no qualitative difference to the results. One still gets enhanced diffusion parallel to the flow, which is normal (i.e., not anomalous). Of course, the numerical value of the effective diffusion coefficient will vary between the two cases. As discussed in Section 1, this holds only if the system size in the longitudinal dimension is finite. Otherwise, one can get anomalous diffusion. However, the case of finite transverse system size is one of great experimental interest. Just as for normal Taylor diffusion, these results hold at long times, long compared to the time necessary for the diffusing particles to sample the entire transverse velocity gradient.

If $k$ is the transition rate and $\eta$ is the layer thickness, then $D_{\text{mol}}=k\eta^2$ is the molecular diffusion coefficient in the continuum limit of a Pearson walk. More strictly stated, one goes to the continuum limit by sending $\eta\to 0$, $k\to\infty$ so that $k\eta^2$ is fixed; this fixed value is interpreted as $D_{\text{mol}}$. For the persistent walk (without superposed flow), one takes the limit $v\to\infty$, $r\to\infty$ in such a way that $v^2/(2r)$ is fixed[6,7]; this fixed value is interpreted as $D_{\text{mol}}$. Hence, our result (24) has precisely the same form as the classical Taylor result when expressed in terms of $D_{\text{mol}}$. The difference is in the interpretation of $D_{\text{mol}}$ in terms of mesoscopic parameters of the model.

We have studied not only the effects of persistence of the effective diffusion coefficient, but also the next-order (constant) term in the asymptotic behavior of $\langle(\delta x)^2\rangle$. We have calculated the result in detail only for the Pearson-walk case. As was the case for the leading term in that case, the formal expression in terms of the eigenvalues and eigenfunctions of the transition matrix can be written solely in terms of the initial probability distribution, the steady-state probability distribution, and the transition states. It is not necessary to actually solve the eigenvalue problem.

For the leading term in $\langle(\delta x)^2\rangle$ in the persistent case, Eq. (12), we have not found it possible to reduce it to a form depending exclusively on the transition rates, steady-state probabilities, and the flow profile $u_j$, mainly because of the appearance of a complicated inverse matrix. To get numerical results for this term will require explicit computation of the eigenvalues and eigenvectors of the transition matrix **K**.

In summary, the replacement of a Pearson walk by a persistent walk makes quantitative, but not qualitative, changes in Taylor dispersion.

## APPENDIX

To derive the results (22) and (23) one starts from the dimensionless equations (20). Using the definition for the reduced probability density [see Eq. (18)] and the constraints imposed by the boundary conditions, one finds after integrating over $\rho$

$$\partial_\theta(\rho, \theta) = -\mu \int_0^1 d\rho\, f(\rho)\, \partial_\zeta p \tag{A1}$$

Substituting the expansion for $p$, Eq. (21), and keeping powers of $\mu$ up to second order, one gets Eq. (22).

One evaluates $p^0$ and $p^1$ by using Bogoliubov's functional hypothesis,[17] Eq. (19). From the boundary conditions,[15] $\partial_\rho g^0 = 0$, $p^0 = n(\xi, \theta)$. Furthermore,

$$(\partial_\theta p)^1 = -\partial_\rho g^1 - f(\rho)\, \partial_\zeta p^0 \tag{A2}$$

$$(\partial_\theta g)^1 = -\partial_\rho p^1 - \left(\frac{2rL}{v}\right) g^1 \tag{A3}$$

After some manipulations one finds that

$$(\partial_\theta p)^1 = -\int d\zeta' \frac{\delta p^0}{\delta n(\zeta', \theta)} \int_0^1 dz\, f(z) \frac{\partial p^0}{\partial \zeta'}$$

Substituting this value of $(\partial_\theta p)^1$ on the left-hand side of (A2) and solving for $g^1$, one finds

$$g^1 = -\int_0^\rho d\rho' \,[f(\rho') - \bar{f}]\, \partial_\zeta n(\zeta, \theta) + c(\zeta, \theta) \tag{A4}$$

From the boundary conditions, $c(\zeta, \theta)$ is zero.

Finally, $p^1$ is found from Eq. (A3), i.e., by setting $(\partial_0 g)^1 = 0$ and substituting $g^1$ from the value given in (A4). After integration one finds

$$p^1(\zeta, \rho, \theta) = \left(\frac{2rL}{v}\right) \partial_\zeta n(\zeta, \theta) \times \left\{ \int_0^\rho d\rho' \int_0^{\rho'} dz \, [f(z) - \bar{f}] - \int_0^1 d\rho \int_0^\rho d\rho' \int_0^{\rho'} dz \, [f(z) - \bar{f}] \right\} \tag{A5}$$

Substituting $p^0 = n(\zeta, \theta)$ and (A5) in Eq. (22) and transforming to the original variables with dimensions $(x, y, t)$, we finally get (23).

## ACKNOWLEDGMENTS

G.S.-C. is grateful for support from a U. S. Department of Education scholarship for Graduate Assistance in Areas of National Need. We also thank the referees for calling our attention to refs. 8, 10, and 11.

## REFERENCES

1. N. G. van Kampen, Composite stochastic processes, *Physica* **96A**:435–453 (1979).
2. G. I. Taylor, Dispersion of soluble matter in solvent flowing slowly through a tube, *Proc. R. Soc. Lond. A* **219**:186–203 (1953); Conditions under which dispersion of a solute in a stream of solvent can be used to measure molecular diffusion, *Proc. R. Soc. Lond. A* **225**:473–477 (1954).
3. J. C. Giddings and H. Eyring, A molecular dynamic theory of chromatography, *J. Phys. Chem.* **59**:416–421 (1955).
4. C. Van den Broeck and R. M. Mazo, Exact results for the asymptotic dispersion of particles in $n$-layer systems, *Phys. Rev. Lett.* **51**:1309–1312 (1983); The asymptotic dispersion of particles in $N$-layer systems, *J. Chem. Phys.* **81**:3624–3634 (1984).
5. G. I. Taylor, Diffusion by continuous movements, *Proc. Lond. Math. Soc.* **20**:196–212 (1921).
6. S. Goldstein, On diffusion by discontinuous movements, and on the telegraph equation, *Q. J. Mech. Appl. Math.* **IV**:129–156 (1950).
7. M. Kac, A stochastic model related to the telegrapher's equation, *Rocky Mountain J. Math.* **4**:497–509 (1974).
8. G. Matheron and G. de Marsily, Is transport in porous media always diffusive? A counterexample, *Water Resource Res.* **16**:901–917 (1980).
9. R. M. Mazo and C. Van den Broeck, The asymptotic dispersion of particles in $N$-layered systems: Periodic boundary conditions, *J. Chem. Phys.* **86**:454–459 (1987).
10. B. Gaveau and L. S. Schulman, Anomalous diffusion in a random velocity field, *J. Stat. Phys.* **66**:375–383 (1992).
11. E. Ben-Naim, S. Redner, and D. ben-Avraham, Bimodal diffusion in power-law shear flows, *Phys. Rev. A* **45**:7207–7213 (1992).

12. R. Czech and K. W. Kehr, Depolarization of rotating spins by random walks on lattices, *Phys. R. B.* **34**:261–277 (1986).
13. R. M. Mazo and C. Van den Broeck, Spectrum of an oscillator making a random walk in frequency, *Phys. Rev. B* **34**:2364–2374 (1986).
14. G. H. Weiss and R. J. Rubin, Random walks: Theory and selected applications, in *Advances in Chemical Physics*, Vol. LII, Section IIA4 (1983).
15. G. Soto-Campos, Ph.D. thesis, University of Oregon (1995).
16. G. Soto-Campos, Unpublished.
17. N. N. Bogoliubov, In *Studies in Statistical Mechanics*, Vol. I, J. de Boer and G. E. Uhlenbeck, eds. (North-Holland Amsterdam 1962); N. N. Bogolubov, Jr., B. I. Sadovnikov, and A. S. Shumovsky, *Mathematical Methods of Statistical Mechanics of Model Systems* (CRC, Boca Raton, Florida, 1994), p. 172.
18. R. Aris, On the dispersion of a solute in a fluid flowing through a tube, *Proc. R. Soc. Lond. A* **235**: 67–77 (1956).
19. R. M. Mazo, On the Green's function for a one-dimensional random walk, *Cell Biophys.* **11**:19–24 (1987).