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Exact Results for the Asymptotic Dispersion of Particles in *n*-Layer Systems

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A fluid flows parallel to the strata of an n-layer stratified system. Particles suspended in the fluid are carried along with the flow, and additionally make random jumps into neighboring strata, where the flow velocity is different. The spatial dispersion of the particles in the flow direction, for long times, is calculated exactly for arbitrary n, jump rates, and velocity field. The result is applied to a variety of phenomena, e.g., chromatography, Taylor diffusion, and random walks.

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In this Letter, we present a versatile and widely applicable method for calculating the effective diffusion coefficient for a system of particles flowing in a layered system, the direction of flow being perpendicular to the layer normals. The model, and our solution of it, has a large number of different applications, e.g., to chromatography, to the problem of dispersion in porous media, to Taylor diffusion, and to random-walk problems themselves.

We consider a system of n layers or channels. The layers are planar, parallel to the x-z plane. In each layer i, $i=1,\dots,n$, fluid is flowing in the x direction with velocity u_i. Particles suspended in the fluid are carried along with the local flow velocity. In addition, they perform a random walk between the layers. The transition rates for going from layer i to the adjacent layers $i+1$ and $i-1$ will be denoted by k_i^+ and k_i^-, respectively. We consider here reflecting boundary conditions, i.e., $k_n^+ = k_1^- = 0$; for convenience, we define $k_0^+ = k_{n+1}^- = 0$. We will calculate the exact longitudinal dispersion, $\langle \delta x^2(t)\rangle$ in the long-time limit and then show the relevance of the result for the problems mentioned above.

The probability densities $P(x,i,t)$ of observing a suspended particle at the position x in layer i at time t obey the following set of balance equations:

$$\partial_t P(x,i,t) = \{-\partial u_i/\partial x - k_i^+ - k_i^-\}P(x,i,t) + k_{i+1}^- P(x,i+1,t) + k_{i-1}^+ P(x,i-1,t). \tag{1}$$

One may also consider the concentration $c(x,i,t)$ which is the probability $P(x,i,t)$ times the (constant) total number of particles. The quantity we are interested in is the dispersion in the flow direction x,

$$\langle \delta x^2(t)\rangle = \sum_{i=1}^{n} \int dx [x - \langle x(t)\rangle]^2 P(x,i,t), \tag{2}$$

where

$$\langle x(t)\rangle = \sum_{i=1}^{n} \int dx\, x P(x,i,t) = \sum_{i=1}^{n} \mu_i(t). \tag{3}$$

From (1) one easily obtains the following equation for $\langle \delta x^2(t)\rangle$:

$$\partial_t \langle \delta x^2(t)\rangle = 2\sum_{i=1}^{n} [\mu_i(t) - \langle x(t)\rangle P_i(t)] u_i, \tag{4}$$

where $P_i(t)$ is the probability of being in layer i at time t irrespective of the horizontal position x,

$$P_i(t) = \int dx\, P(x, i, t). \tag{5}$$

The equation obeyed by $P_i(t)$ is obtained by integrating Eq. (1) over x,

$$\partial_t P_i(t) = \sum_{j=1}^{n} K_{ij} P_j(t), \tag{6}$$

where the matrix K is given by

$$K_{ij} = -(k_i^+ + k_i^-)\delta_{ij} + k_{i-1}^+ \delta_{i-1,j} + k_{i+1}^- \delta_{i+1,j}. \tag{7}$$

Multiplication of (1) by x and subsequent integration over x yields the equation for $\mu_j(t)$,

$$\partial_t \mu_i(t) = \sum_{j=1}^{n} K_{ij}\,\mu_j(t) + u_i P_i(t). \tag{8}$$

Equations (7) and (8) can be solved in terms of the right and left eigenvectors, X_{ij} and Y_{ji}, corresponding to the eigenvalues, λ_j, of the matrix K. In particular, one known the eigenvector X_{i1} associated with $\lambda_1 = 0$:

$$X_{i1} = P_i^{\mathrm{st}} = N k_1^+ k_2^+ \cdots k_{i-1}^+ k_{i+1}^- \cdots k_n^-, \tag{9}$$

where N is the normalization constant $(\sum_i P_i^{\mathrm{st}} = 1)$. We suppose that the random walk being considered is irreducible; otherwise one would have sets of layers which do not communicate with each other and the problem would break up into separable subproblems. Then one obtains the following equation for the dispersion:

$$\partial_t \langle \delta x^2(t)\rangle = -2\sum_{i,j=1}^{n} u_i P_i^{\mathrm{st}} u_j P_j^{\mathrm{st}} G_{ij} + B \tag{10}$$

where B denotes terms decaying exponentially in time, and G_{ij} is the Green's function,

$$G_{ij} = \sum_{r=2}^{n} \frac{Y_{ri}\,Y_{rj}}{\lambda_r}. \tag{11}$$

The remaining problem is to obtain an explicit expression for the Green's function. Fortunately, this problem has been solved by Herrick[1] in quite a different context (the distribution of electrons over the manifold of excited states of an atom). His method is easily adapted to our problem, although the algebra is rather tedious. We only quote the final result for the dispersion:

$$K \equiv \lim_{t\to\infty} \langle \delta x^2(t)\rangle / 2t$$
$$= \sum_{l=1}^{n-1} \Big[\sum_{i=1}^{n} \sum_{j=1}^{l} (u_i - u_j) P_i^{\mathrm{st}} P_j^{\mathrm{st}}\Big]^2 / P_l^{\mathrm{st}} k_l^+. \tag{12}$$

Note that the sum over l may be taken to include $l+n$ since this term is zero anyway.

Equation (12) is the fundamental result of this Letter. In the remaining part, we illustrate how it can be applied to various problems.

For $n=2$, the general expression (12) reduces to the well known result for the dispersion of particles on a chromatographic column.[2] The case $n=3$, with $u_1 = u_3 = 0$, corresponds to a chromatographic problem with two different types of absorbates, represented by layer 1 and layer 3, respectively.[3] Layer 2 corresponds to the mobile phase with velocity $u_2 = u$. The dispersion reads $(k_1^+ = k_1,\ k_3^- = k_3)$

$$K = u^2\, \frac{k_1 k_3 (k_2^- k_3^2 + k_2^+ (k_1^2))}{(k_1 k_2^+ + k_3 k_2^- + k_1 k_3)^3}. \tag{13}$$

In the limit as $k_2^- \to 0$ or $k_2^+ \to 0$, one recovers, of course, the $n=2$ result. The case of $n=4$ can be applied to the problem of an active absorbent which can exist in two different forms in the mobile phase.[4]

The result (12) can be simplified further when applied to some typical problems occurring in the problem of dispersion in stratified porous media. In the limit that the adsorption-desorption equilibrium is established rapidly in each layer, the flow velocities, u_i, and the exchange rates, $k_i = k_i^+ = k_i^-$, depend on the layer index, i, in the same way, since they have, as common origin, the adsorption-desorption equilibrium in that layer. Let us define ρ_i, $0 < \rho_i < 1$, as the fraction of nonadsorbed molecules in each layer. It is also convenient to introduce $r_i = 1/\rho_i$ and $\bar{r} = \sum r_i / n$. If k and u are the exchange rate and flow velocity in the absence of adsorption ($\rho_i = 1$), then one has

$$k_i = k\rho_i = k/r_i; \quad u_i = u\rho_i = u/r_i. \tag{14}$$

From (12) and (14) one obtains

$$K = \frac{u^2}{nk\bar{r}} \sum_{l=1}^{n-1} \Big[\sum_{j=1}^{l} (1 - r_j/\bar{r})\Big]^2. \tag{15}$$

This simple exact result can be used for the calculation of the long-time dispersion of both free and adsorbed particles in porous stratified media, instead of the phenomenological or numerical calculations used heretofore.[5] Note that a result identical in form to (15) is obtained if one assumes that the transition rates k_i are independent of i.

In order to consider the continuum limit, we introduce the thickness of a layer, η, and the vertical coordinate $y = i\eta$ and define $P(x,y,t) = P(x,i,t)/\eta$. Furthermore, we write

$$k_i^{\pm} = k_i \pm \epsilon_i. \tag{16}$$

We then take the limit $n\to\infty$, $k_i\to\infty$, $\epsilon_i\to\infty$, and $\eta\to 0$ in such a way that the products $n\eta=L$, $k_i\eta^2=D(y)$, and $\epsilon_i\eta=w(y)$ remain constant. In this limit, the set of equations (1) goes over into the equation

$$\partial_t P(x,y,t)=\left\{-\frac{\partial u(y)}{\partial x}-\frac{\partial v(y)}{\partial y}+\frac{\partial}{\partial y}D(y)\frac{\partial}{\partial y}\right\}P(x,y,t), \tag{17a}$$

with reflecting boundary conditions

$$\frac{\partial P(x,y,t)}{\partial y}=0 \text{ at } y=0,\ y=L. \tag{17b}$$

We have introduced the flow velocity in the y direction,

$$v(y)=2w(y)-D(y)/dy. \tag{18}$$

Equation (17) describes the problem of Taylor diffusion[6] between two parallel reflecting plates with $u(y)$ the flow velocity of the fluid, $v(y)$ the sedimentation velocity perpendicular to the boundary plates, and $D(y)$ the diffusion coefficient. By the limit procedure outlined above, we obtain for the corresponding Taylor diffusion coefficient

$$K=\int_0^L dy\,\frac{[\int_0^L dy'\int_0^{y'}dy''\{u(y')-u(y'')\}P^{\mathrm{st}}(y')P^{\mathrm{st}}(y'')]^2}{P^{\mathrm{st}}(y)D(y)}, \tag{19}$$

with

$$P^{\mathrm{st}}(y)=N\exp[\int^y dy'v(y')/D(y')], \tag{20}$$

and N a normalization constant.

This general result can be shown to reduce to results known from the literature in several particular cases. For example, in Taylor's original problem,[6] where $v=0$ and $D(y)=D$, independent of y, Eq. (19) becomes

$$K=\frac{1}{LD}\int_0^L dy\{\int_0^y dy'[\bar{u}-u(y')]\}^2, \tag{21}$$

with

$$\bar{u}=\frac{1}{L}\int_0^L u(y')dy', \tag{22}$$

which is easily shown to be equivalent to a previous result for K in terms of a series expansion.[7] In the more general case $v(y)=0$, but arbitrary $D(y)$, (19) reduces to the result obtained by Bowden,[8] following Taylor's original arguments.

For the particular case $u_i=\delta_{i,r}$, one has $x(t)=\tau_r$, where τ_r is the residence time in the rth layer given a total elapsed time t. In this case, Eq. (12) gives the exact long-time dispersion of the residence time for a state in a general one-dimensional random walk (or a birth and death process) with reflecting boundary conditions,

$$\lim_{t\to\infty}\frac{\langle\delta\tau_r^{\,2}|t\rangle}{2t}=\sum_{l=1}^{n-1}(P_r^{\mathrm{st}})^2[\sum_{j=1}^{l}P_j^{\mathrm{st}}-\theta_{l,r}]^2/P_l^{\mathrm{st}}k_l^{+}. \tag{23}$$

Here $\theta_{l,r}$ is the discrete Heaviside function ($\theta_{l,r}=1$ for $l\geq r$ and zero otherwise). As far as we know, the result (23) is new.

In a similar way, by taking $u_i=\delta_{i,r}+\delta_{i,r'}$ one can obtain $\langle\delta\tau_r\,\delta\tau_{r'}|t\rangle$. We just mention here the result of (23) in the limit of large n and for the simple case when all the transition rates are equal to k,

$$\langle\delta\tau_r^{\,2}|t\rangle\approx\frac{2t}{k}\left[\frac{1}{3}-\frac{r}{n}\left(1-\frac{r}{n}\right)\right]. \tag{24}$$

Hence $\langle\delta\tau_r^{\,2}|t\rangle$ is independent of n for large n (for a fixed fractional distance, r/n, in the chain). Equation (24) is valid for $n\gg 1$, $t\gg n/k$.

In a subsequent paper, we shall give more details and further applications of the theory.

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