DISPERSION OF PARTICLES IN STRATIFIED SYSTEMS*

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Stochastic models for Taylor dispersion in systems which are stratified or layered in a direction normal to the direction of flow are reviewed. Applications to systems with random velocities in the several layers, to system with random transition rates between the layers, and to fractal systems are sketched. Generalizations to two dimensional strata normal to the flow are indicated, and some specific examples given.

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1. Introduction

When a solvent flows through a tube, any solute will be carried along with the flow. One would expect that solute originally uniformly spread across the tube cross section would be drawn out into a parabolic profile as time evolves (*cf.* Fig. 1(a)). In fact, something different happens. The solute moves downstream at the average velocity of the solvent, but its distribution broadens; the amount of broadening is proportional to the elapsed time (*cf.* Fig. 1(b)). This phenomenon was discussed by G.I. Taylor [1] and is named Taylor diffusion or Taylor dispersion after him.

Taylor dispersion can be very important in practical applications. One such is the measurement of diffusion coefficients in the liquid state [2].

The physical reason for this surprising phenomenon is that the solute diffuses transversely across the tube cross section as it flows longitudinally down the tube. (Longitudinal diffusion also occurs, of course, but its effect is negligible and we shall neglect it in this paper.) Thus the solute samples the entire velocity distribution, and hence moves, on the average, with the

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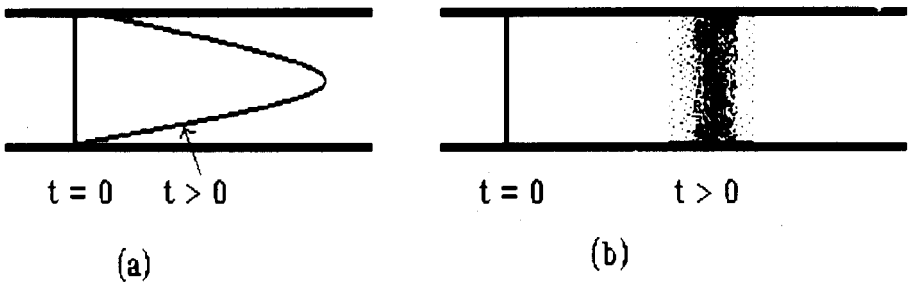


Fig. 1. (a) The concentration profile of the solute for flow in a tube as it would be in the absence of Taylor diffusion. (b) The concentration profile as it is in fact, after sufficiently long times.

mean fluid velocity. However, diffusion is a random process, and a solute particle will spend random amounts of time at different points of the velocity profile. This induces a dispersion in the distribution of the solute particles.

We have studied a discrete version of this process [3]. The transverse direction consists of N discrete layers. In each layer, j, fluid is flowing with velocity u_j. Solute particles make a random walk between the layers with transition rates $k_j^{\pm}$; the plus/minus sign refers to the rates for moving from j to $j \pm 1$ respectively. The scheme is depicted in Fig. 2.

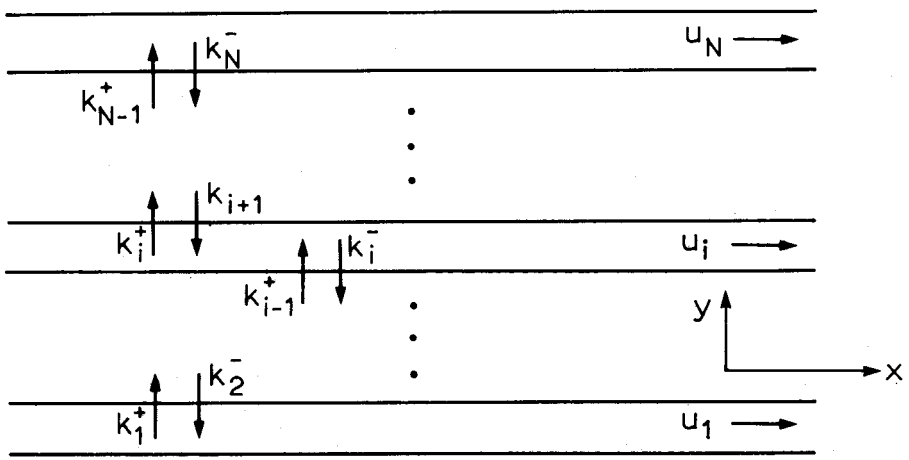


Fig. 2. A schematic representation of the stratified flow system. Layers 1, N, and one interior layer are shown.

Classical Taylor dispersion is recovered in the limit $N \to \infty$. In the other extreme limit, $N = 2$, one obtains a stochastic model for chromatography [4]. One layer corresponds to the stationary phase, with $u = 0$, and the other to the mobile phase.

Taylor dispersion is an example of a class of stochastic processes called compound stochastic processes [5]. One has two processes, $\boldsymbol{X}$ and $\boldsymbol{Y}$, whose probability distributions obey the evolution equations

$$\begin{aligned} \partial_t y &= F(y) \\ \partial_t x &= G(x, y). \end{aligned} \tag{1}$$

That is, $\boldsymbol{Y}$ evolves independently, and $\boldsymbol{X}$ evolves in a way which depends on $\boldsymbol{Y}$. In the present case, $\boldsymbol{Y}$ is the transverse coordinate of a solute particle and $\boldsymbol{X}$ is its longitudinal position which depends on $\boldsymbol{Y}$ since the fluid velocity depends on $\boldsymbol{Y}$.

It is important to realize that the solute particles, the solvent, and the layers may be metaphorical. The model may be applied to several rather different physical situations with a proper reinterpretation of the variables. We shall see below some examples of such reinterpretation.

This paper is a summary of talks given by the author at the *4th Conference on Statistical Physics* at Zakopane, September, 1991. It is primarily a review of work done in collaboration with C. Van den Broeck, though a few new results are included.

2. Formulation of the problem

The probability of finding a solute particle in layer j, $1 \leq j \leq N$, is denoted by $P(x, j; t)$ and is assumed to be governed by the master equation

$$\partial_t P(x, j; t) = \sum_{j=1}^{N} \left[-\frac{\partial}{\partial x} u_i \delta_{ij} + K_{ij} \right] P(x, j; t), \tag{2}$$

where u_j is the velocity in the j'th layer and $\boldsymbol{K}$ is the matrix of transition rates between the layers. $\boldsymbol{K}$ is given by

$$\begin{pmatrix} -k_1^+ & k_2^- & 0 & \dots 0 \\ k_1^+ & -\left(k_2^- + k_3^+\right) & k_3^- & \dots 0 \\ 0 & k_3^+ & -\left(k_3^- + k_4^+\right) & \dots 0 \\ \cdot & \cdot & \cdot & \cdots \end{pmatrix}. \tag{3}$$

The quantities of interest for us are the average values

$$\begin{aligned} \langle x(t) \rangle &= \sum_j \int dx x P(x, j; t), \\ \langle \delta x^2(t) \rangle &= \sum_j \int dx \left(x - \langle x \rangle\right)^2 P(x, j; t) \end{aligned} \tag{4}$$

and $\langle \exp(ix(t)) \rangle$. To get these quantities, we must solve Eq. (2) which will involve us in the study of the Green's function $G(z) = (K - z1)^{-1}$. Eq. (2) can be attacked in two ways. The first, which has been described in [3], is to take its fourier-laplace transform in space and time. One can then immediately read off expressions for the laplace transforms of the moments

$$\langle \widetilde{\delta x^n}(z) \rangle = \sum_{i,j} \left[\frac{n!}{z - K} \left(U \frac{1}{z - K} \right)^n \right]_{i,j} p_j^{st}, \tag{5}$$

where $G(z)$ is the Green's function defined above, and U is $\mathrm{diag}(u_1 - \bar{u}, u_2 - \bar{u}, \cdots, u_N - \bar{u})$. $\bar{u}$ is the mean flow velocity, $\bar{u} = \sum u_i p_i^{st}$. Note that the Green's function G is a rational function of z since the system it describes is finite dimensional. p_i^{st} is the steady state ($t \to \infty$) value of $\int P(x, j; t) dx$.

From (5) and a tauberian theorem for laplace transforms, one may read off the asymptotic behaviour of $\langle \delta x^n(t) \rangle$ for large t.

$$\langle x(t) \rangle = \bar{u}t, \tag{6}$$

$$\sigma^2 \equiv \langle \delta x^2(t) \rangle \to 2D_{\mathrm{eff}} t + O(1), \tag{7}$$

$$\langle \delta x^{2m}(t) \rangle \to (2m!)\sigma^{2m}/2^m m! + O(t^{m-1}), \tag{8}$$

$$\langle \delta x^{2m+1}(t) \rangle \to O(t^m), \tag{9}$$

where

$$D_{\mathrm{eff}} = \sum_i (u_i - \bar{u}) \widetilde{G}_{ij}(0)(u_j - \bar{u}) p^{st}. \tag{10}$$

Here $\widetilde{G}$ is the modified Green's function [6]

$$\widetilde{G}_{ij}(z) = G_{ij}(z) - p_i^{st} \delta_{ij}/z. \tag{11}$$

The expression (10) for D_{eff} can be written directly in terms of the input data of the problem, without explicitly constructing the Green's function

$$D_{\mathrm{eff}} = \sum_{r=1}^{N} \frac{\left[\sum_{i=1}^{r} (u_i - \bar{u}) p_2^{st} \right]^2}{k_r^+ p_r^{st}}. \tag{12}$$

The expression for the third moment, $S = \lim \langle \delta x^3 \rangle / 6t$ can also be written in terms of the original variables of the problem [3].

With the aid of these moments, one may construct the Gram–Charlier series [7] for the distribution function $P(x, t) = \sum_j P(x, j, t)$

$$P(x, t) = \frac{\exp\left(\delta x^2 / 2\sigma^2\right)}{(2\pi\sigma^2)} \left[1 + \Phi_e \left(\frac{\delta x}{\sigma} \right) + \Phi_o \left(\frac{\delta x}{\sigma} \right) \right]. \tag{13}$$

Here, Φ_e and Φ_o are series of even and odd hermite polynomials, respectively. The coefficients of these series are determined uniquely by the moments, Eq. (6–9) and vanish as t^{-1} and $t^{-1/2}$ respectively. Consequently, the distribution function is gaussian for long times.

There is another way to obtain these results which may have a bit more physical appeal. This uses the Chapman–Enskog method familiar from the kinetic theory of gases; it is a technique for the elimination of fast variables. Suppose one has an equation of the form

$$\partial_t f(x,y,t) = (A_y + \mu B_x) f, \tag{14}$$

where the operator A_y operates on the variable y only, and the operator B_x on the variable x only. However, B_x may depend parametrically on y. μ is a small parameter. In our case, A_y is the matrix K; it operates on a finite dimensional space. B_x is the operator $\sum u_i \partial/\partial x$, and the parameter $\mu = a/l$ where a is the width of the tube and l is a measure of the length of the inhomogeneity. A_y is furthermore supposed to be a "divergence-like" operator, in the sense that $\int A_y g(y) dy = 0$ for all g. In our case, the matrix K has this property since its column sums vanish.

We are interested in the function

$$n(x,t) = \int f(x,y,t) dy. \tag{15}$$

In the case at hand, n corresponds to the function $P(x,t)$.

Now let us assume that $f(x,y,t)$ is a functional of n, and depends on t only through the dependence of $n(x,t)$ on t.

$$f(x,y,t) = F[x,y|n(x,t)] \quad t \gg 1/\mu. \tag{16}$$

This is the famous Boguliubov assumption [8]. Now let us expand

$$f = f^{(0)} + \mu f^{(1)} + \mu^2 f^{(2)} + \ldots \tag{17}$$

and require that

$$\int f^{(0)} dy = n; \quad \int f^{(m)} dy = 0 \quad \text{for } m > 0. \tag{18}$$

Integrating (14) with respect to y, one finds, to second order in μ

$$\partial_t n(x,t) = \mu \int dy B_x f^{(0)} + \mu^2 \int dy B_x f^{(1)}. \tag{19}$$

Now, expanding (14) in powers of μ and equating like powers

$$\partial_t f^{(0)} = A_y f^{(0)}. \tag{20}$$

Since

$$\partial_t f^{(0)}(x,y,t) = \int \frac{\delta F^\circ}{\delta n(t)} \frac{\partial n(z,t)}{\partial t} dz. \tag{21}$$

Hence $\partial f^0/\partial t$ is of first order in μ and consequently $f^{(0)}$ obeys the homogeneous equation

$$A_y f^{(0)} = 0, \tag{22}$$

while $f^{(1)}$ obeys the equation

$$\partial_t f^{(1)} = A_y f^{(1)} + B_x f^{(0)}. \tag{23}$$

The solution to (22) is

$$f^{(0)}(x,y,t) = p(y)n(x,t), \tag{24}$$

where p is a solution of $A_y p = 0$, normalized to unity. The solution to (23) is

$$\begin{aligned} f^{(1)} &= f_0^{(1)} + \int G\left(y|y'\right) \gamma(y',x,t) dy', \\ \gamma(y',x,t) &= p(y') \left[B_x n(x,t) - \int du B_x p(u) n(x,t) \right], \end{aligned} \tag{25}$$

where $G(y|y')$ is the Green's function for the operator A_y and $f_0^{(1)}$ is a solution of the homogeneous equation $A_y f_0^{(1)} = 0$. Because of (18) we obtain

$$\int f_0^{(1)} dy = - \int G\left(y|y'\right) \gamma(y',x,t) dy dy'. \tag{26}$$

Putting (25) in (19) we finally obtain

$$\partial_t n = \mu \int dy p(y) B_x n(x,t) + \mu^2 \int B_x f^{(1)} dy \tag{27}$$

When the explicit forms of the operators are introduced, (27) becomes the convective diffusion equation

$$\partial_t n = D_{\text{eff}} \left(\frac{\partial^2 n}{\partial x^2} \right) - \bar{u} \frac{\partial n}{\partial x} \tag{28}$$

with D_{eff} given by (12).

Note that the Green's function used in (25) is often a Green's function "in the extended sense" [6] since, as is the case here, 0 may be an eigenvalue of the operator A_y.

The advantage of this method of approach is that it yields directly the evolution equation for the longitudinal velocity distribution. Furthermore, it takes some of the mystery out of Taylor's original derivation, which always seemed a bit of a *tour de force*. The disadvantage is that moments higher than the second of the distribution function are not given correctly.

The continuum limit of the stratified model is just Taylor's original model (for simple shear flow rather than Poiseuille flow), and the other extreme limit, $N = 2$, corresponds to chromatography. Our results give precisely the well known results in these two limiting cases; this is a valuable check. The general case of N strata has an interest of its own, as we shall now try to show.

First, let us consider the question of the correlation of residence times in a random walk on a lattice. Suppose that the lattice has N sites, and let τ_j be the time that the walker spends on site j in a given realization of the walk. We would like to know $\langle \tau_j \rangle$ and $\langle \tau_j \tau_k \rangle$ for a given elapsed time t. These correlations may be immediately read off from the results already obtained.

Clearly we have $x = u_1\tau_1 + u_2\tau_2 + \ldots + u_N\tau_N$. Hence $\langle \tau_j \rangle$ is the coefficient of u_j in $\langle x \rangle$. From (6) this is $p_j^{\text{st}} t$, hardly a surprising result. Less trivial is $\langle \tau_i \tau_j \rangle$ which is the coefficient of $u_i u_j$ in $\langle \delta x^2 \rangle$. But this is simply related to (7); the final result is

$$\langle \delta\tau_j \delta\tau_k \rangle = 2t \sum_{r=1}^{N} \sum_{i=1}^{r} \sum_{\ell=1}^{r} \frac{\left(p_j^{\text{st}} t - \delta_{ji}\right)\left(p_k^{\text{st}} - \delta_{k\ell}\right) p_i^{\text{st}} p_\ell^{\text{st}}}{k_r^+ p_r^{\text{st}}} \tag{29}$$

Another application is to the theory of motional narrowing in the ESR spectra of one dimensional lattices, when the individual sites of the lattice have random energy level splittings, or equivalently, random frequencies. As is well known [9], the shape of a spectral line is proportional to the correlation function of the Heisenberg operator which couples the spectroscopic system to the radiation field.

$$I(\omega) \propto \int e^{i\omega t} \phi(t) dt,$$

$$\phi(t) = \langle O^+(t) O(0) \rangle. \tag{30}$$

We may write $\phi(t) = \langle \exp(ix(t)) \rangle$, where $x(t)$ is the phase of the operator O.

$$x(t) = \omega_1 t_1 + \omega_2 t_2 + \ldots + \omega_N t_N, \tag{31}$$

ω_j being the splitting on site j.

This is precisely the Taylor dispersion problem which we have been considering, with the ω's taking the place of the u's, and $\langle \exp(ix) \rangle$ taking the place of $\langle \delta x^2 \rangle$ as the quantity to be calculated.

Czech and Kehr [10] have studied this problem for the case of an infinite lattice. There are appreciable differences between the infinite and finite cases in the limit of long times. In the former, the random walker is always visiting new sites. In the latter, the sites visited have in general been visited previously, and consequently the site splittings are correlated in time.

There are two ways to attack the line shape problem. The first is to calculate $\phi(t)$ and fourier transform the result. The second is to transform to frequency space immediately, and evaluate the resulting formulae. Both methods have been used [11].

For times $t \gg N^2 \tau_c$, $\phi(t)$ has been shown to be given by

$$\phi(t) = \left[\frac{N \sinh \Theta \cosh \Theta}{\sinh N\Theta \cosh N\Theta} \right]^{1/2} \exp\left(-\frac{\omega_p^2 t^2}{2N} \right), \tag{32}$$

where Θ is defined by $\sinh^2 \Theta = \omega_p^2 \tau_c t / 2N$. ω_p is the frequency dispersion of the site splittings, $\langle \delta\omega^2 \rangle$, and τ_c is k^{-1}. When $\omega_p^2 \tau_c t / 2N \gg 1$ this simplifies to

$$\phi(t) = \sqrt{N} \left[\frac{N}{2\omega_p^2 \tau_c t} \right]^{n-1/2} \exp\left(\frac{\omega_p^2 t^2}{2N} \right). \tag{33}$$

Note that an infinite system, $N \to \infty$, never reaches this long time limit.

If either N or τ_c are very large, ϕ will have decayed to negligible values before the asymptotic regime is ever reached; (32) is then useless. On the other hand, there exist realizable circumstances in which the asymptotic formula, (32), is valid over most of the interesting time range.

Fig. 3 shows a computation of $\phi(t)$ by simulation of the random walk for a lattice of 50 sites, $\alpha = \omega_p \tau_c = 0.005$. The asymptotic formula (32) is shown for comparison; the agreement is excellent. Fig. 4 shows results of the same calculation for $N = 16$ and larger values of α. Again the results are satisfactory, but less so at the larger values of α.

The second approach to the calculation of the line shape is to multiply Eq. (1) by $\exp(ix)$ and integrate with respect to x. The result is, of course, an equation for $\phi(t)$. Introducing the matrix $\boldsymbol{\Omega}$ by $\Omega_{jk} = \omega_j \delta_{jk}$, one finds

$$\langle \exp\left(ix(t)\right) \rangle = \sum_{jk} \left[\exp\left(i\left[\Omega + K\right] t \right) \right]_{j,k} \mu_k, \tag{34}$$

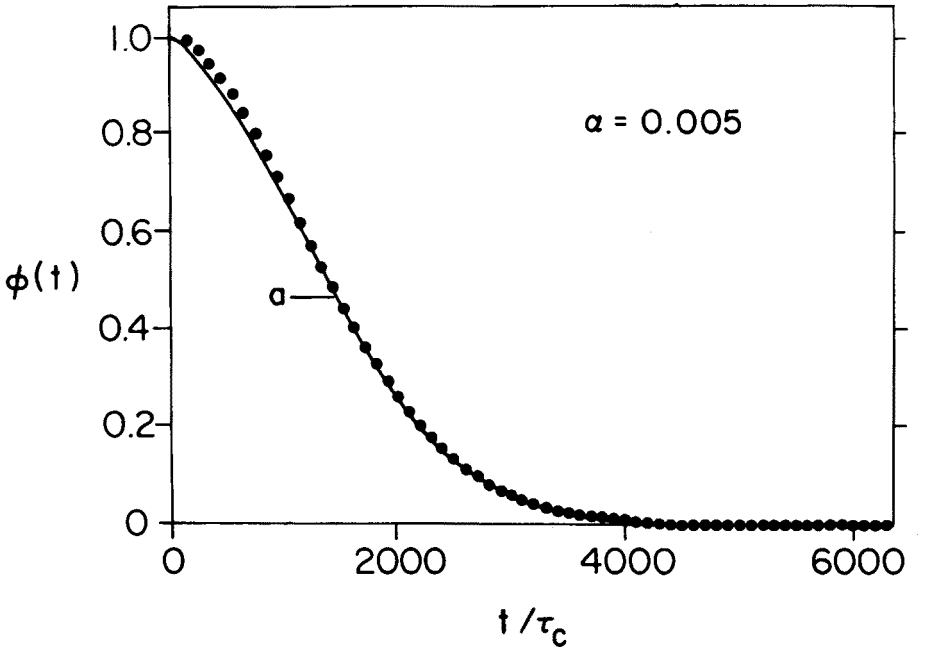


Fig. 3. The correlation function , Eq. (30), for $N = 50$, $\alpha = \omega_p \tau_c = 0.005$. The circles are simulation results; the solid line, marked a, is Eq. (32).

where μ_j is $\int \exp(ix) P(x, j; 0) dx$. This formal solution may be formally fourier transformed, yielding, after averaging over the random frequencies.

$$I(\omega) \propto \sum_{(j,k)} \langle [i\omega \mathbf{1} + i\boldsymbol{\Omega} + \boldsymbol{K} - \omega_r \mathbf{1}]_{jk} \rangle \mu_k, \tag{35}$$

ω_r is a phenomenological damping parameter, $\omega_r \tau_c \ll 1$, introduced to take account of slow relaxation processes not accounted for in the basic model [12]. If it were not for the extremely slow decay of $\phi(t)$ in the one dimensional model this *ad hoc* modification of the theory would not be necessary.

Equation (35) does not solve the problem of the line shape in the sense of an analytical solution; finding the inverse matrix and carrying out the indicated average are still formidable problems. Nevertheless, it does form the basis for a useful numerical procedure. This is: generate a set of frequencies, $\{\omega_j\}$ using a random number generator appropriate to some assumed probability distribution, invert the matrix numerically, and perform the sum. This must be done for a large number of sets of the ω's, and the results averaged. We have done this.

In each case, the resulting line shape for each realization of the ω's was lorentzian, but the line centers and line widths varied from trial to trial.

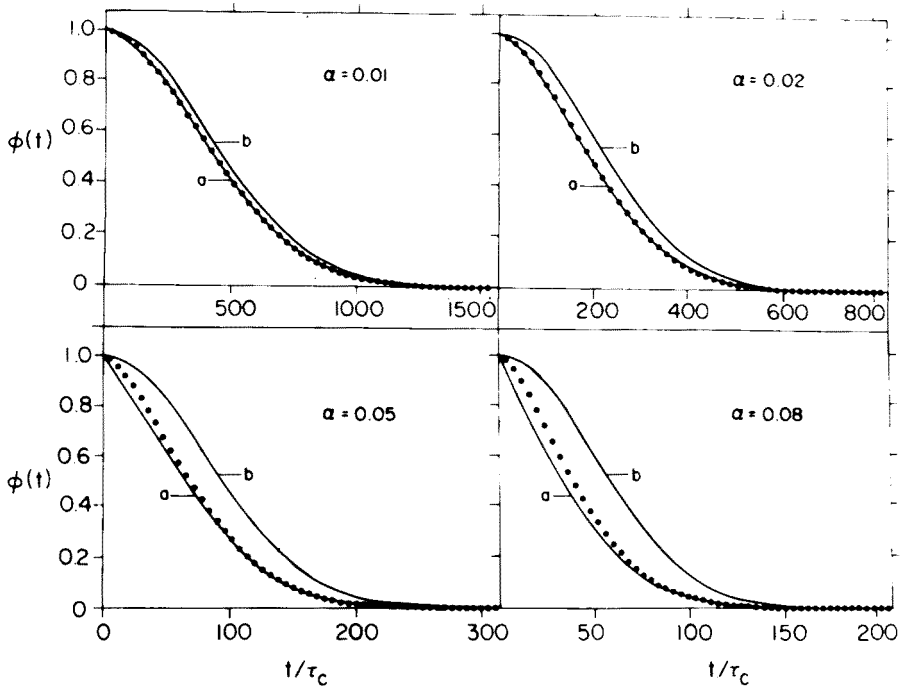


Fig. 4. The correlation function, Eq. (30), for $N = 16$ and various values of $\alpha = \omega_p \tau_c = 0.005$. The circles are simulation results. The line marked a is Eq. (32) and the line marked b is a gaussian with the same initial curvature as Eq. (32).

When the results of many trials were averaged, the resulting line shape was gaussian. This is shown in Fig. 5.

For an infinite lattice in one dimension, $\phi(t)$ decays as $\exp(-at)$ for long times, while behaving like $\exp\left(-bt^{3/2}\right)$ for shorter times. We have seen that, for a finite lattice, the asymptotic behaviour is given by (33). In higher dimensions this slow decay is not seen. This is clearly associated with the fact that a random walk in one (and two) dimension has probability one of returning to its origin, while in three and higher dimensions this probability is less than one (about 0.35). Thus, the finite size of the system plays an essential role in one dimension, and possibly in two. The theory of the two dimensional case, a particle hopping on a surface, has not been worked out from the point of view of the present theory.

Let us conclude this section by just mentioning that analogous results to those which have been obtained in the case of reflecting boundaries can also be derived for the case of periodic boundary conditions [13]. This is convenient for the transition to $N \to \infty$, and also because there are some physical situations in which periodic boundary conditions are appropriate

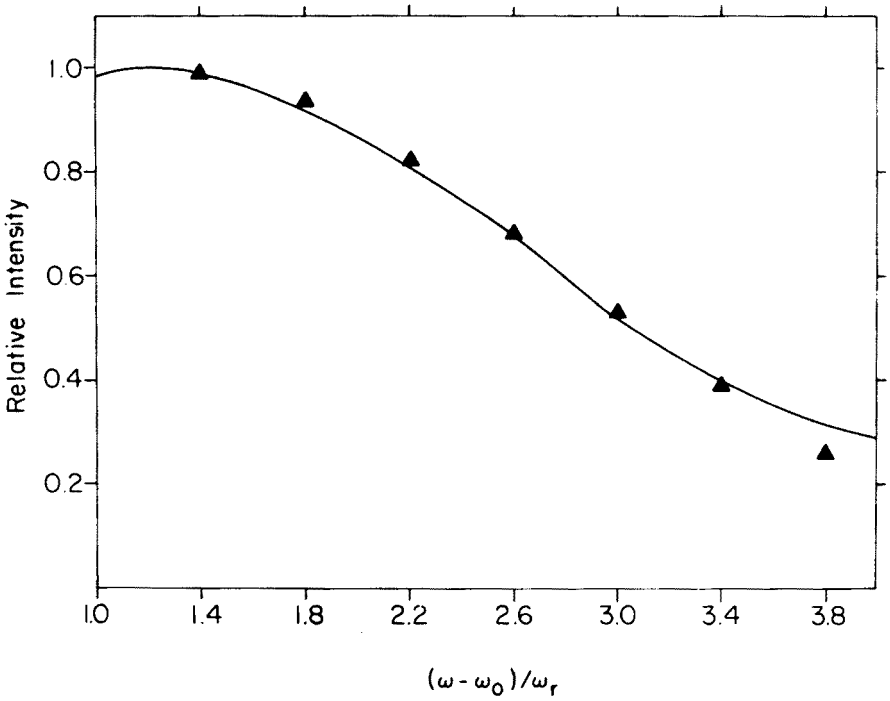


Fig. 5. The intensity, normalized to unity at the center of the line, for 20 samples at $N = 18$. The circles are a gaussian fit to the curve.

in their own right.

3. Random systems

So far we have been mostly discussing situations in which the parameters of the system were deterministic. There are degrees of randomness which can affect problems of this type. They can be categorized as randomness in space, time, velocity, and transition rates.

Randomness in velocities has already been discussed in the spectroscopic problem of the last section, in which the site frequencies were random variables. Another example is the case of a system with periodic boundary conditions where the velocities in the layers are independent random variables, $\langle u_i u_j \rangle = \langle u^2 \rangle \delta_{ij}$. This is the same as the spectroscopic model, except that we are here treating it as a diffusion problem, and are interested in $\langle \delta x^2(t) \rangle$. This model can be solved exactly [13] with the result that

$$\left\langle \widetilde{\delta x^2}(z) \right\rangle = \frac{2\langle u^2 \rangle}{p^2 (p + 4k)^{1/2}}. \tag{36}$$

This implies, in real time, that

$$\langle \delta x^2(t) \rangle \underset{t\to\infty}{\longrightarrow} \frac{2}{3}\frac{\langle u^2 \rangle}{(2\pi k^2)^{1/2}}(2kt)^{3/2}. \tag{37}$$

Note that this example exhibits an anomalous dispersion. The width of the distribution grows as $t^{3/2}$, not as t.

So far, we have been assuming that the jumps between strata have an exponential distribution in time; that is the probability of a jump in time dt is kdt. Van den Broeck has studied an interesting variant with a different waiting time distribution [14]. Suppose that the steps take place at discrete times instead of continuously; a waiting time of length 2^r between successive steps occurs with probability 2^{-r}. Waiting times which are not powers of 2 have zero probability. This is analogous to the Saint Petersburg game of probability theory [15]. He shows that the mean number of steps in time t behaves, for long times as

$$\langle n(t) \rangle \sim \frac{t}{\ln_2 t}. \tag{38}$$

In a normal random walk (in discrete time), the number of steps is, of course, just t. This is an example of random time in a dispersion problem.

Very often, the transverse structure of a flow system is not known, or is exceptionally complex, so that the only information one has about it is statistical. This is what we meant by the phrase "random in space" used above. Consider a system which is regular, in some sense, along the flow direction, but is irregular transverse to the flow direction. As an example, one might think of a tube, uniform in cross section, but for which each cross section has a fractal structure, the same for each cross section. To visualize this, think of a "Toblerone tube", each cross section of which is a Sierpinski gasket. What would Taylor dispersion look like on such a structure?

To study this one must first understand diffusion on a fractal lattice. Diffusion on a fractal has been studied a great deal [16], but mostly from the point of view of determining the exponent in the relation $\langle \delta x^2 \rangle \propto t^{\Theta}$. For our purposes, the relevant question is not this, but, what is the diffusion equation on a fractal substrate? O'Shaughnessy and Procaccia [17] have given an answer to this question for the envelope of the concentration profile. The actual profile will have a very complex structure; it will be a multifractal, a distribution on a fractal. However, when this complex multifractal is smoothed over regions small compared to macroscopic distances, a smooth distribution is expected, which O'Shaugnessy and Procaccia argue obeys the evolution equation

$$\frac{\partial \Psi}{\partial t} = \frac{1}{r^{D-1}}\frac{\partial}{\partial r}\left(K r^{-\Theta} r^{D-1} \frac{\partial}{\partial r} \right) \Psi. \tag{39}$$

Here D is the fractal dimension of the substrate, and $Kr^{-\Theta}$ is the diffusion coefficient. Note that the diffusion coefficient is not a diffusion constant; it is distance dependent. Eq. (39) is supposed to be a description of diffusion from a point source.

To adapt this result to a description of Taylor diffusion one must generalize it in two ways. First, one adds a new dimension, orthogonal to those described by the radius vector r; call this new coordinate z. Then add the term $u_0 f(r/a)\partial\Psi/\partial z$ to the left hand side of (39); this describes the convection in the z direction. One now has a convective diffusion equation.

The second generalization which must be made is to replace the point source with a more general source distribution; a sheet source would be more appropriate for present purposes. It is not clear at the present time how this should be done, so we restrict ourselves here to the case of a point source on the axis of a cylindrical tube, the cross section of which has a fractal structure of fractal dimension D.

The Chapman–Enskog method can be used to eliminate the transverse degrees of freedom, as described in Section 2. The calculation is rather tedious, and we just quote here the result. One obtains a conventional convective diffusion equation

$$\frac{\partial\Psi}{\partial t} + u_0 f\left(\frac{r}{a}\right)\frac{\partial\Psi}{\partial z} = K_{\text{eff}}\frac{\partial^2\Psi}{\partial z^2}, \tag{40}$$

where the effective diffusion coefficient is given by

$$K_{\text{eff}} = K_0 - \frac{u_0^2 a^{\Theta+2}}{K_0} D^2 \int_0^1 \rho^{D-1} f(\rho)\,d\rho$$

$$\times\Big(\int_0^1 x^{D-1}dx \int_0^x y^{1+\Theta-D}dy \int_0^y \alpha(s)ds - \int_0^\rho x^{1+\Theta-D}dx \int_0^x \alpha(s)ds\Big), \tag{41}$$

$$\alpha(s) = s^{D-1}\Big(f(s) - D\int_0^1 \rho^{D-1} f(s)ds\Big).$$

(We have used K_0 and K_{eff} for the diffusion and effective diffusion coefficients here in order to save D for fractal dimension.) Note that, in the limiting case $D = 2$, $\Theta = 0$, D_{eff} becomes $u_0^2 a^2/192K_0$ for a parabolic velocity profile. This is just what Taylor's original work predicts.

It is unsatisfactory that this result has only been derived for the special case of a point source on the axis of a tube. The generalization to an arbitrary initial distribution is an open problem.

Another class of problems which might be called randomness in space are cases where the transition rates between the layers, $k_j^{\pm}$, are themselves random variables. The effective diffusion coefficient, D_{eff}, is then also a random variable. What is its distribution function? What are its mean and variance?

The formula for D_{eff}, (12), is a rather complicated function of the $k^{\pm}$. In order to see what to expect, we have calculated $\langle D_{\text{eff}} \rangle$, $\langle \delta D_{\text{eff}}^2 \rangle$, and estimated the distribution of D_{eff}, by simulation. This work was done by Mr. Gerardo Soto Campos. We took a system of 10 layers and picked the $18k^{\pm}$ by a random number generator. D_{eff} was then calculated by Eq. (12) and the results of many such trials were averaged.

In the first example, we took the $18k_{ij}^{\pm}$ to be independent dichotomic random variables taking the values 0.7 and 0.5 with probability $1/2$. The absolute values of the k's are unimportant, as is the absolute value of the maximum velocity. These numbers merely set the scale for D_{eff} and do not affect either the shape of the D distribution or the relative dispersion. The velocity profile chosen was a linear one. 900 sets of k's were generated.

A histogram showing the empirical distribution of D_{eff} is shown in Fig. 6. Note that the distribution is asymmetrical about its maximum, and cannot be fit by a gaussian. It can be fit reasonably well by a "shifted gamma" distribution

$$\phi(x) = \frac{1}{\beta^{\alpha}\Gamma(\alpha)}(x-10)^{\alpha-1}\exp\left(\frac{-(x-10)}{\beta}\right), \tag{42}$$

where α and β are parameters determined by the empirical fit and normalization. The fit is characterized by a χ^2 of 15.54 with 9 degrees of freedom; at the .05 confidence level with 9 degrees of freedom, $\chi^2 = 16.92$.

Another experiment used a gaussian distribution of the k's,with the center and width of the distribution chosen so that no negative k's occurred. 300 trials of a 5 layer system were generated. Here, the distribution of D_{eff} was gaussian; $\chi^2 = 8.7$ compared to the expected χ^2 of 11 for 5 degrees of freedom at the 0.05 confidence level.

It would be interesting to see if one could understand these simulation results in terms of the theory of random matrices, since D_{eff} is essentially related to the Green's function of the matrix $\boldsymbol{K}$, Eq. (10). On the other hand, most studies of random matrices of which we are aware have studied matrices with certain symmetries (hermitean, orthogonal, *etc.*). The $\boldsymbol{K}$ matrices which we deal with have completely independent elements off the diagonal, while the sums of the elements in each column must vanish. Consequently the diagonal elements are not independent. As far as we know, the statistical properties of such matrices have never been studied. Such a study would seem quite worthwhile.

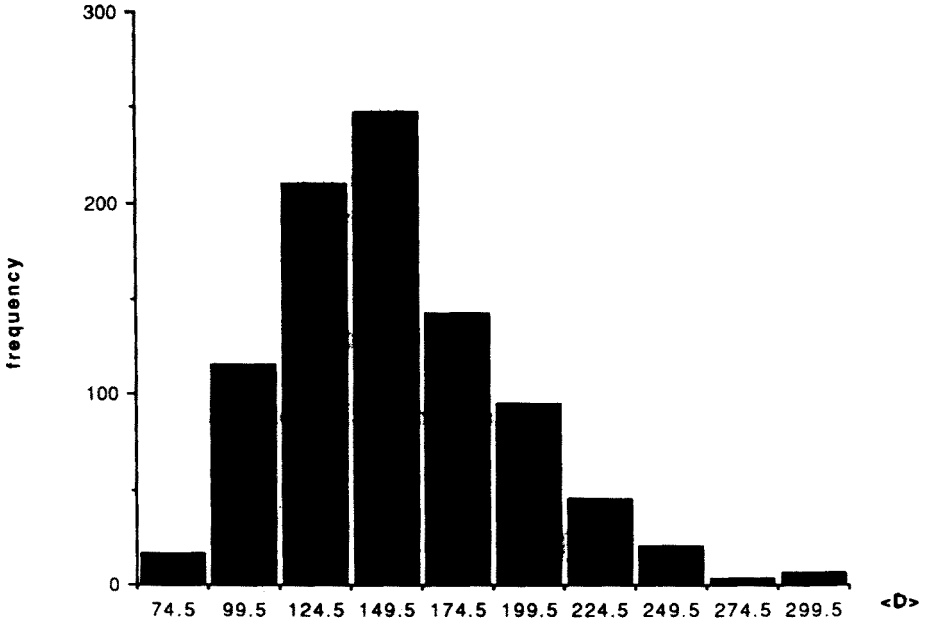


Fig. 6. The frequency distribution of the effective diffusion coefficient for dichotomic transition rates, $k = 0.5$ or 0.7 with probability 0.5: 900 samples.

For the nonrandom case when all k's are equal, it is easy to see from (12) that $D_{\text{eff}} \propto 1/k$. Is it also true that in the random case $D_{\text{eff}} \propto \langle 1/k \rangle$? To investigate this for the case of dichotomous variables, we repeated the calculation for various values of p, the probability that $k = 0.5$. 300 sets of k's for each p were computed, and we looked at the quantity $D_{\text{eff}}/\langle k^{-1} \rangle$. Indeed, $D_{\text{eff}}/\langle k^{-1} \rangle$ was constant within the error of the simulation. $D_{\text{eff}}/\langle k^{-1} \rangle = 82.38$, $0 \leq p \leq 1$, with a standard deviation of 1.02. This fluctuation is of the same order of magnitude as the standard deviation for a fixed value of p. We have not performed an analysis of variance, but the proportionality of D_{eff} to $\langle 1/k \rangle$ appears to hold well. More numerical experiments are needed to determine if this proportionality to $\langle 1/k \rangle$ is the rule or an accident of the case considered.

So far we have been considering only one dimension transverse to the flow. Even in the fractal case the model was effectively one dimensional since we considered only radial diffusion. There are however, situations in which the dimension of the space in which the random walk is taking place is greater than one. One example has already been mentioned, spectroscopy of mobile particles on random surfaces. Another possibility is Taylor dispersion in a two dimensional array of channels.

To study such problems, it is necessary to have some information on

lattice Green's functions in dimensions higher than one. For an infinite lattice, there is a considerable amount of information available about these functions [18]. For a finite lattice, there is very little information.

Let us consider the problem of a random walk on a two dimensional lattice with transition rates κ in the x direction and λ in the y direction. The situation is sketched in Fig. 7. The transition matrix for this case is denoted by $\boldsymbol{K}^{(2)}$; the superscript denotes the dimension of the underlying lattice. $\boldsymbol{K}^{(2)}$ is simply related to $\boldsymbol{K}^{(1)}$ for the one dimensional case. In fact

$$\boldsymbol{K}^{(2)} = K^{(1)'} \otimes I'' + I' \otimes K^{(1)''}, \tag{43}$$

where the prime and double primes denote the horizontal and vertical directions.

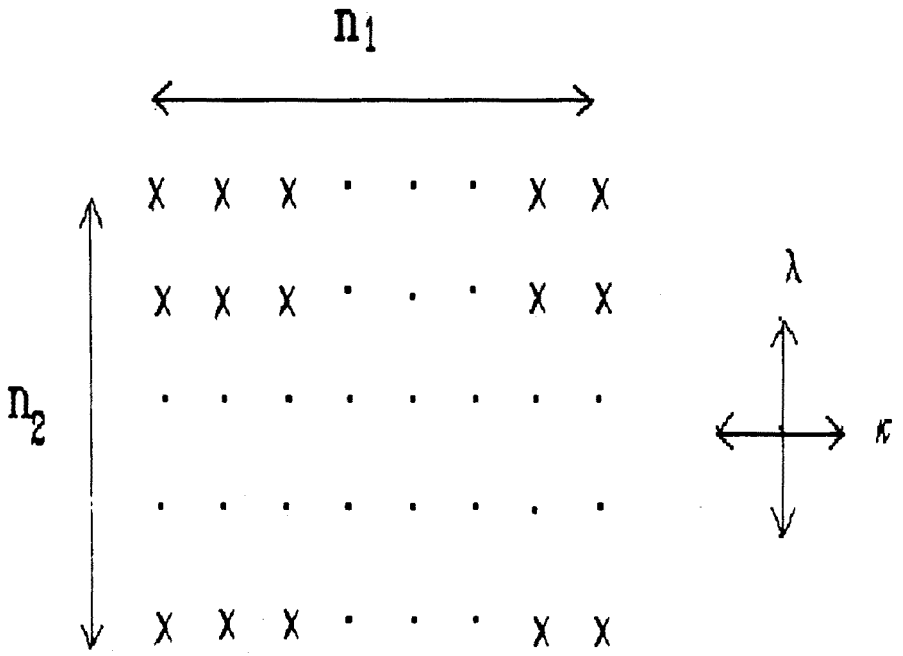


Fig. 7. A two dimensional lattice with different transition rates in the two directions.

Schwalm and Schwalm have noted [19] that, when (43) holds, it is possible to write the Green's function in terms of the Green's functions for the one dimensional case, a fact which we had already observed for the particular case at hand.

To see this, we write down the bilinear formula for the Green's function

$$G^{(2)}(Z) = \sum_{\alpha',\alpha''} \frac{X^{(1)}_{\alpha'} X^{(1)}_{\alpha''} Y^{(1)}_{\alpha'} Y^{(1)}_{\alpha'}}{Z - \lambda_{\alpha'} - \lambda_{\alpha''}}. \tag{44}$$

As above, the prime and double prime refer to the x and y directions respectively and $X^{(1)}_{\alpha'}$ and $X^{(1)}_{\alpha''}$ are the right eigenvectors, $Y^{(1)}_{\alpha'}$ and $Y^{(1)}_{\alpha''}$ the left eigenvectors, $\lambda_{\alpha'}$ and $\lambda_{\alpha''}$ the eigenvalues of $K^{(1)'}$ and $K^{(1)''}$ respectively. Carrying out the sum over α' or α'' , one obtains immediately

$$\begin{aligned} G^{(2)}(z) &= \sum_{\alpha'} X^{(1)}_{\alpha'} Y^{(1)}_{\alpha'} G^{(1)}(z - \lambda_{\alpha'}) \\ &= \sum_{\alpha''} Y^{(1)}_{\alpha''} Y^{(1)}_{\alpha''} G^{(1)}(z - \lambda_{\alpha''}). \end{aligned} \tag{45}$$

Thus the double sum over $n_1 n_2$ terms has been reduced to a single sum over either n_1 or n_2 terms. When either n_1 or n_2 is small, *i.e.* when the lattice is a narrow strip, this is a major simplification. It would be desirable to have the entire Green's function in simple closed form, but, at the present time, we do not have such a convenient formula.

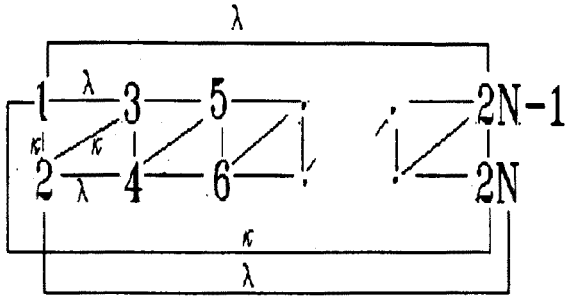
As another example of a narrow strip lattice, let use consider the lattice of $2N$ sites shown in Fig. 8(a). Sites 1 and 2 are connected to site $2N$, while site 1 is also connected to site $2N - 1$. It is clear that this is a model for random walk on a one dimensional lattice with both nearest neighbor and next nearest neighbor transitions, with rates κ and λ respectively, and with periodic boundary conditions. This model does not fall in the class of models described by (43) because of the "diagonal hopping". Nevertheless, it can be evaluated precisely. The eigenfunctions and eigenvalues of K are known, and hence (44) can be written

$$G^{(\text{period})}_{p,p'}(z) = \frac{1}{2N} \sum_{j=0}^{2N-1} \frac{\exp\left(\frac{i\pi j(p-p')}{N}\right)}{z + 4\lambda \sin^2(\pi j/N) + 4\kappa \sin^2(\pi j/2N)}. \tag{46}$$

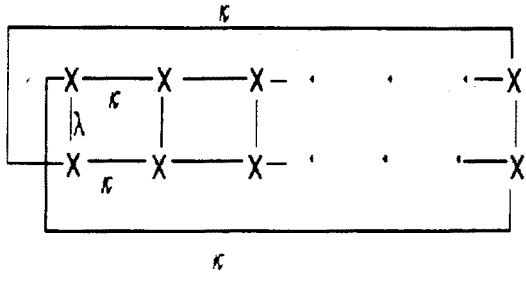
The sum over j can be carried out explicitly by a complex variable technique, integrating a suitable function over a contour enclosing all of the poles of (46). We omit the technical details and quote here the result

$$\begin{aligned} G^{(\text{period})}_{p,p'}(z) = \frac{1}{4\lambda} \Bigg(& \frac{\cosh\beta_1 (N - |p - p'|)}{\sinh N\beta_1 \sinh\beta_1 (\cosh\beta_1 - \cosh\beta_2)} \\ & - \frac{\cosh\beta_2 (N - |p - p'|)}{\sinh N\beta_2 \sinh\beta_2 (\cosh\beta_1 - \cosh\beta_2)} \Bigg) \end{aligned}$$

$$\cosh\left\{\begin{matrix}\beta_1 \\ \beta_2\end{matrix}\right\} = \frac{1}{2}\left(-\frac{\kappa}{2\lambda}(\pm)\left(\frac{\kappa^2}{4\lambda^2} + \frac{1}{\lambda}(z + 2\kappa + 4\lambda)\right)^{1/2}\right). \tag{47}$$



(a)



(b)

Fig. 8. (a) A narrow two dimensional lattice isomorphic to a one dimensional walk with nearest and next-nearest neighbor transitions; periodic boundary conditions. (b) A two dimensional lattice on a Moebius strip.

With reflecting boundary conditions, we have the same picture, but with the external connections erased. The same technique yields

$$G^{(\mathrm{ref})}_{p,p'}(z) = \frac{1}{2\lambda(\cosh\beta_1 - \cosh\beta_2)} \times \left(\frac{\cosh\beta_1 \left(N - \max(p,p') + \frac{1}{2}\right) \cosh\beta_1 \left(\min(p,p') - \frac{1}{2}\right)}{\sinh\beta_1 \sinh N\beta_1} - \frac{\cosh\beta_2 \left(N - \max(p,p') + \frac{1}{2}\right) \cosh\beta_2 \left(\min(p,p') - \frac{1}{2}\right)}{\sinh\beta_2 \sinh N\beta_2} \right). \quad (48)$$

As a final amusing application of these ideas, we give the Green's func-

tion for random walk on a (narrow) Moebius strip; the lattice is shown in Fig. 8. The result is given in terms of one dimensional Green's functions, and is

$$G^{(\text{Möb})}_{p,p'}(z) = G^{(\text{per})}_{p,p';2N}(z+2\lambda) + \tfrac{1}{2}\left(G^{\text{per}}_{p,p';N}(z) - G^{\text{per}}_{p,p';N}(z+2\lambda)\right). \quad (49)$$

The Green's functions on the left hand side are one dimensional, as indicated by the superscript. They refer to a periodic lattice, with period $2N$ or N, as indicated in the subscripts, and are known in closed form [20], [21].

4. Discussion

We have reviewed the theory of dispersion in stratified systems. The theory has a wide range of applications, from chromatography to spectroscopy. It applies to physical situations described by degrees of freedom which can be divided into two groups. In one group lie a set of variables which evolve independently of all of the others, usually in a stochastic way. In the other set lie the rest of the variables, evolving in a deterministic manner, but modulated by the values of the stochastic degrees of freedom.

For the case when the subspace of stochastic variables is one dimensional, and there is no other underlying randomness in the problem, the theory has been developed rather far. When there is additional randomness, we have mostly numerical simulations to guide us in understanding the phenomena. This is not universally true. In the problem of motional narrowing it has been possible to go rather far analytically. Also, when the subspace of stochastic degrees of freedom has dimension higher than one, current knowledge is meager. I believe that progress in these two areas, randomness, and higher dimensions, will yield fruitful results.

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