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A DISCRETE RANDOM WALK MODEL FOR DIFFUSION IN MEDIA WITH DOUBLE DIFFUSIVITY

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Abstract

Diffusion in the presence of high-diffusivity paths is an important issue of current technology. In metals, high-diffusivity paths are identified with dislocations, grain boundaries, free surfaces and internal microcracks. In pourous media such as rocks, fissures provide a system of high-flow paths. Recently, based on a continuum approach, these phenomena have been modelled, resulting in coupled systems of partial differential equations of parabolic type for the concentrations in bulk and in the high-diffusivity paths. This theory assumes that each point of the medium is simultaneously occupied by more than one diffusion or flow path. Here a simple discrete random walk model of diffusion in a medium with double diffusivity is given. The continuous version of this model gives rise to precisely the coupled system of partial differential equations obtained from the continuum approach. For the discrete model three problems are considered : the unrestricted particle, the particle with reflecting barriers at the end points, and the particle moving between absorbing barriers. For the source solutions of the continuous model an approximate expression is obtained for the total concentration. Numerical results are given which compare this approximate solution with an exact expression obtained previously.

1. Introduction

Diffusion in a homogeneous, isotropic, isothermal, rigid medium with a single family of diffusion paths is described by the classical diffusion equation, based on Fick's second law of diffusion, namely

$$\frac{\partial c}{\partial t} = D\nabla^2 c, \quad D > 0, \tag{1.1}$$

where $c(\mathbf{x}, t)$ is the concentration and D the diffusion coefficient (see, for example, Crank [7]). For diffusion in an ideal medium, but with two families of diffusion paths, Aifantis [2, 3] has proposed the following coupled system for the concentrations in each path:

$$\frac{\partial c_1}{\partial t} = D_1 \nabla^2 c_1 - k_1 c_1 + k_2 c_2 \quad \text{and} \quad \frac{\partial c_2}{\partial t} = D_2 \nabla^2 c_2 + k_1 c_1 - k_2 c_2, \tag{1.2}$$

where D_1, D_2, k_1 and k_2 are all constants for which physical arguments indicate the following inequalities:

$$D_1 > 0, \quad D_2 > 0, \quad k_1 > 0 \quad \text{and} \quad k_2 > 0. \tag{1.3}$$

For example, (1.2) is proposed to describe diffusion in a polycrystalline metal where the diffusivity in the grain boundary space is several orders of magnitude larger than the bulk diffusivity.

The above system is strictly valid only for diffusion problems. However, formally similar equations have been proposed by Barenblatt *et al.* [5] to describe the flow of liquid in rocks which are assumed to consist of both systems of pores and fissures. These equations also arise from "multiporosity theory" (see Aifantis [1]). This theory describes diffusion and flow in a medium possessing more than one family of diffusion or flow paths. Thus, for example, the theory may be applicable to the seepage of water in soils where additional flow paths arise from the soil's cracking or possibly from old root and worm channels. In Aifantis and Hill [4] and Hill and Aifantis [12] both qualitative mathematical results and solutions of specific boundary value problems are given for the system (1.2) with the inequalities (1.3). We remark that related qualitative studies are also given in [8, 10, 13, 15]. The purpose of this paper is to consider simple problems arising from a discrete random walk model of diffusion in a medium with two distinct families of diffusion paths. The continuous development of this model results in equations (1.2).

The discrete random walk model giving rise to the classical diffusion equation (1.1) is well known (see, for example, Prabhu [14]). Briefly the situation is as follows. A particle is random walking on the integers such that at integral instants in time, a move to the right is made with probability p and to the left with probability q, where $p+q = 1$. If $u_{k,n}$ denotes the probability the particle is at position k at time n then, for an unrestricted particle,

$$u_{k,n+1} = pu_{k-1,n} + qu_{k+1,n} \quad \text{for } n \geqslant 0. \tag{1.4}$$

We now let the jumps be of length Δx and the time interval between jumps Δt; then in the limit as Δx and Δt tend to zero, $u_{k,n}$ is approximately equal to $f(x,t)\,dx$ and (1.4) becomes

$$f(x, t+\Delta t) = pf(x-\Delta x, t) + qf(x+\Delta x, t). \tag{1.5}$$

From Taylor's theorem we have

$$\Delta t \frac{\partial f}{\partial t} = \frac{(p+q)}{2} (\Delta x)^2 \frac{\partial^2 f}{\partial x^2} - (p-q)\, \Delta x \frac{\partial f}{\partial x}, \tag{1.6}$$

and thus, for the free particle ($p = q = \frac{1}{2}$), the classical diffusion equation (1.1) emerges provided Δt and Δx tend to zero in such a way that $\Delta t/(\Delta x)^2$ approaches the finite limit $(2D)^{-1}$. This simple formal connection, which can be made mathematically rigorous, is an important link in understanding diffusion processes.

In the following section we describe a discrete random walk model which gives rise to the coupled equations (1.2) in the continuous limit. We generalize the above classical model by assuming that the particle moves along one of two distinct paths and that at each jump it not only can move either to the left or to the right but also has the possibility of transition to the other path. Apart from providing a simple model for the underlying mechanism, this approach has additional advantages. For example, inequalities such as (1.3) are immediate and need not be derived by *ad hoc* physical arguments. Moreover, guided by the central limit theorem, we are led to an approximate solution of (1.2) which is in agreement with asymptotic formulae given in Aifantis and Hill [4]. This approximate solution can be justified directly from (1.2) and demonstrates clearly departures from the classical expression which are not apparent in the asymptotic results given by Aifantis and Hill [4].

The first sections of the paper deal with aspects of the discrete model. This model is formally similar to one proposed by Barnett [6] for the flow of liquids or gases through packed columns. In fact the model given here is mathematically more complex and consequently the number of problems that can be solved explicitly are limited. In Section 3 we obtain the mean and variance of the position of an unrestricted particle. In Section 4 we obtain the stationary probabilities for a particle with reflecting barriers at 0 and a. Physically these barriers correspond to walls of the container. In Section 5 we obtain the probabilities of absorption at 0 (particle escape), given that both 0 and a are absorbing barriers. In Section 6 the continuous version of the model is considered. In particular, the coupled system of equations (1.2) are deduced and the implications of the continuous form of the results of Section 3 are discussed. The system of coupled partial differential equations for more than two diffusion paths is also discussed briefly.

2. Discrete model for a medium with two distinct diffusion paths

We consider a single particle random walking on the integers on the infinite straight line. In the continuum approach "multiporosity theory" and for a medium with double diffusivity, Aifantis [1–3] assumes that each point of space is simultaneously occupied by two distinct diffusion or flow paths. We therefore consider the infinite line to consist of two paths subscripted by 1 and 2 which we might visualize as two strands of a string. We allow the particle to move along either of these paths but in addition we allow the possibility of a transition from one path to the same position on the other path. If the particle is in path $i, i = 1, 2$, we suppose that at each jump the particle moves one step to the right with probability p_i, one to the left with probability q_i, remains in position with probability r_i and each of these outcomes is assumed to take place within the same path. However, we also assume the particle has probability s_i of occupying the same position on the other path. Thus, at each jump, only one of four possible outcomes can occur. We have, therefore,

$$p_i + q_i + r_i + s_i = 1, \quad i = 1, 2, \tag{2.1}$$

and we shall also assume that the various probabilities are independent of the position of the particle.

We make the following observations for this model. The random movement of a particle in a medium is referred to as diffusion if the randomness is attributed to the particle and to percolation if the randomness is due to the nature of the medium. As noted by Frisch and Hammersley [11], this distinction is not always a precise classification. Clearly, if we allow our probabilities to be position dependent, then the model is more appropriate to the phenomenon of percolation rather than that of diffusion. With these comments in mind we shall for definiteness, in the present model, consider the various probabilities as parameters attributed to the particle rather than to the medium. If, at each jump, we allow two additional outcomes, namely taking one step to the left or to the right but on the other path, then in the equations corresponding to (1.2) we generate the so-called "cross-effects" (see Aifantis [2, 3]). This additional complexity will not be considered here. As far as practicable we will leave the probabilities p_i, q_i, r_i and s_i, $i = 1, 2$, subject to (2.1), completely arbitrary. Indeed, special values do not seem to simplify the mathematics significantly. However, the following list provides some important special cases which relate to previous work :

(i) $p_1 = q_1$, $p_2 = q_2$ (free particle, Aifantis [2, 3]),
(ii) $s_1 = s_2$ (equal transition probabilities, Barenblatt *et al.* [5]),
(iii) $p_1 = q_1, p_2 = q_2 = 0$ (diffusion along one path very much greater than along the other).

Finally, we observe that, although the probabilities r_1 and r_2 appear not to enter the calculations in an essential manner, we shall nevertheless retain them nonzero so that the important special case $p_1 = q_1$, $p_2 = q_2$ and $s_1 = s_2$ can be considered without necessarily implying p_1 and p_2 are the same.

We now consider the problem of an unrestricted particle initially at the origin. This problem corresponds to the source solutions for (1.2) given by Aifantis and Hill [4]. We let $u_{k,n}$ denote the probability that the particle is in path 1 at position k at step n. Similarly, we let $v_{k,n}$ denote the probability that the particle is in path 2 at position k at step n. For no barriers we have the forward equations

and
$$\left.\begin{aligned} u_{k,n+1} &= p_1 u_{k-1,n} + r_1 u_{k,n} + q_1 u_{k+1,n} + s_2 v_{k,n} \\ v_{k,n+1} &= p_2 v_{k-1,n} + r_2 v_{k,n} + q_2 v_{k+1,n} + s_1 u_{k,n}, \end{aligned}\right\} \tag{2.2}$$

for all integers k and for integers $n \geqslant 0$. We further suppose that initially the particle is at the origin and is in path 1 with probability u_0 and path 2 with probability v_0, $u_0 + v_0 = 1$, so that we have

$$u_{k,0} = u_0\,\delta_{k0} \quad \text{and} \quad v_{k,0} = v_0\,\delta_{k0}, \tag{2.3}$$

where δ_{ij} is the usual Kronecker delta. We introduce generating functions

$$U_n(z) = \sum_{k=-\infty}^{\infty} u_{k,n} z^k \quad \text{and} \quad V_n(z) = \sum_{k=-\infty}^{\infty} v_{k,n} z^k. \tag{2.4}$$

From (2.3) we have

$$U_0(z) = u_0 \quad \text{and} \quad V_0(z) = v_0, \tag{2.5}$$

while (2.2) becomes

$$U_{n+1}(z) = \pi_1(z)\,U_n(z) + s_2\,V_n(z) \quad \text{and} \quad V_{n+1}(z) = \pi_2(z)\,V_n(z) + s_1\,U_n(z), \tag{2.6}$$

where the functions $\pi_i(z)$, $i = 1, 2$, are defined by

$$\pi_i(z) = p_i\,z + r_i + q_i\,z^{-1}, \quad i = 1, 2. \tag{2.7}$$

If we introduce $U(z,\xi)$ and $V(z,\xi)$ by

$$U(z,\xi) = \sum_{n=0}^{\infty} U_n(z)\,\xi^n \quad \text{and} \quad V(z,\xi) = \sum_{n=0}^{\infty} V_n(z)\,\xi^n, \tag{2.8}$$

then, in the usual way from (2.5) and (2.6), we can deduce

and
$$\left.\begin{aligned} U(z,\xi) &= \frac{s_2\,v_0\,\xi - [\xi\pi_2(z) - 1]\,u_0}{\{[\pi_1(z)\,\pi_2(z) - s_1\,s_2]\,\xi^2 - [\pi_1(z) + \pi_2(z)]\,\xi + 1\}} \\ V(z,\xi) &= \frac{s_1\,u_0\,\xi - [\xi\pi_1(z) - 1]\,v_0}{\{[\pi_1(z)\,\pi_2(z) - s_1\,s_2]\,\xi^2 - [\pi_1(z) + \pi_2(z)]\,\xi + 1\}}. \end{aligned}\right\} \tag{2.9}$$

Thus, in principal, we have formally obtained the probabilistic behaviour of the unrestricted walk. Although from (2.9) we can deduce expressions for $U_n(z)$ and $V_n(z)$, it appears difficult to proceed further. We therefore content ourselves with the mean and variance of the position of the particle at time n, namely

$$\mu_n = \sum_{k=-\infty}^{\infty} k(u_{k,n} + v_{k,n}) \quad \text{and} \quad \sigma_n^2 = \sum_{k=-\infty}^{\infty} (k - \mu_n)^2\,(u_{k,n} + v_{k,n}). \tag{2.10}$$

The calculation of these quantities is extremely long and tedious and therefore the details are confined to a separate section. However, the calculation is worthwhile since, if X_n is the random variable for the position of the particle at time n, then, from two applications of the central limit theorem (Feller [9]), we know that $(X_n - \mu_n)/\sigma_n$ is approximately standard normally distributed as n tends to infinity.

3. Mean and variance of the position of an unrestricted particle

The mean and variance of the position of the unrestricted particle can be obtained in a variety of ways. We use (2.6) and derivatives of (2.6), set $z = 1$, and solve the resulting difference equations. The following combinations of the probabilities are important parameters and it is convenient to introduce them here:

$$\theta = 1-(s_1+s_2), \quad e_i = p_i - q_i \quad \text{and} \quad f_i = s_i/(s_1+s_2), \quad i = 1,2. \tag{3.1}$$

In the process of calculating μ_n and σ_n^2 we need to determine expressions for

$$\alpha_n = \sum_{k=-\infty}^{\infty} u_{k,n}, \quad \beta_n = \sum_{k=-\infty}^{\infty} v_{k,n}, \tag{3.2}$$

$$\gamma_n = \sum_{k=-\infty}^{\infty} k u_{k,n}, \quad \delta_n = \sum_{k=-\infty}^{\infty} k v_{k,n} \tag{3.3}$$

and

$$\varepsilon_n = \sum_{k=-\infty}^{\infty} k(k-1)(u_{k,n}+v_{k,n}), \tag{3.4}$$

so that the mean and variance are then given by

$$\mu_n = \gamma_n + \delta_n \quad \text{and} \quad \sigma_n^2 = \varepsilon_n + \mu_n - \mu_n^2. \tag{3.5}$$

For the quantities α_n and β_n we observe from (2.3) and (3.2) that $\alpha_0 = u_0$ and $\beta_0 = v_0$. On setting $z = 1$ in (2.6) and making use of (2.1) we have

$$\alpha_{n+1} = (1-s_1)\alpha_n + s_2\beta_n \quad \text{and} \quad \beta_{n+1} = (1-s_2)\beta_n + s_1\alpha_n. \tag{3.6}$$

At time n the probabilities the particle is in path 1 or path 2 are α_n and β_n, respectively. On noting that $\alpha_n + \beta_n = 1$, we can readily deduce from (3.6) that

$$\alpha_n = f_2 + (u_0 - f_2)\theta^n \quad \text{and} \quad \beta_n = f_1 + (v_0 - f_1)\theta^n. \tag{3.7}$$

Thus we can identify f_2 and f_1 as the probabilities the particle is ultimately in path 1 and path 2, respectively.

In order to determine the mean μ_n, we differentiate (2.6) with respect to z, set $z = 1$, and add the resulting equations. We obtain

$$\mu_{n+1} = \mu_n + e_1 \alpha_n + e_2 \beta_n. \tag{3.8}$$

On observing that $\mu_0 = 0$, we have from (3.7) and (3.8) that

$$\mu_n = nA + B\frac{(1-\theta^n)}{(1-\theta)}, \tag{3.9}$$

where A and B are constants which are defined by

$$A = e_1 f_2 + e_2 f_1 \quad \text{and} \quad B = e_1(u_0 - f_2) + e_2(v_0 - f_1). \tag{3.10}$$

In the calculation of the variance σ_n^2 we differentiate (2.6) twice with respect to z, set $z = 1$, and add the resulting equations. Using (3.2), (3.3) and (3.4) we have

$$\varepsilon_{n+1} = \varepsilon_n + 2e_1 \gamma_n + 2e_2 \delta_n + 2q_1 \alpha_n + 2q_2 \beta_n. \tag{3.11}$$

We therefore need to determine expressions for the quantities γ_n and δ_n. We do this by differentiating the first equation in (2.6) once with respect to z, setting $z = 1$, and making use of the first equation in (3.5). We obtain

$$\gamma_{n+1} = \theta\gamma_n + e_1 \alpha_n + s_2 \mu_n. \tag{3.12}$$

From this equation the first equation in (3.7) and (3.9) we can deduce an expression for γ_n which, together with the first equation in (3.5) and (3.9), yields an expression for δ_n. The final results are as follows :

$$\left.\begin{aligned} &\gamma_n = C + Af_2 n + (nE - C\theta)\theta^{n-1} \\ \text{and}\qquad &\delta_n = C^* + Af_1 n + (nE^* - C^*\theta)\theta^{n-1}, \end{aligned}\right\} \tag{3.13}$$

where the various constants are given by

$$\left.\begin{aligned} C &= f_2(e_1 + B - A)/(1-\theta), & C^* &= f_1(e_2 + B - A)/(1-\theta), \\ E &= e_1 u_0 - f_2(e_1 + B), & E^* &= e_2 v_0 - f_1(e_2 + B). \end{aligned}\right\} \tag{3.14}$$

On using (3.7) and (3.13) in (3.11) we obtain after a long calculation

$$\varepsilon_n = n(n-1)A^2 + 2nF + 2G[1 - n\theta^{n-1} + (n-1)\theta^n]/(1-\theta)^2 + 2H(1-\theta^n)/(1-\theta), \tag{3.15}$$

where the constants F, G and H are given by

$$\left.\begin{aligned} &F = e_1 C + e_2 C^* + q_1 f_2 + q_2 f_1, \\ &G = e_1 E + e_2 E^*, \\ \text{and}\qquad &H = q_1(u_0 - f_2) + q_2(v_0 - f_1) - e_1 C - e_2 C^*. \end{aligned}\right\} \tag{3.16}$$

From the second equation in (3.5), (3.9) and (3.15) we can deduce an expression for the variance σ_n^2. Unfortunately, there appears to be no significant simplications so we shall not give this expression explicitly. We note, however, that the important special case of a free particle $p_i = q_i$, $i = 1, 2$, gives the mean μ_n zero while the variance σ_n^2 is given by

$$\sigma_n^2 = 2(q_1 f_2 + q_2 f_1) n + 2[q_1(u_0 - f_2) + q_2(v_0 - f_1)] (1 - \theta^n)/(1 - \theta). \tag{3.17}$$

We also remark that we can check the above results since in the limit, as $r_i, s_i, i = 1, 2$, tend to zero, and $p_1 = p_2$, we can deduce the mean and variance of the classical random walk, namely $n(p_1 - q_1)$ and $4np_1 q_2$, respectively (see Prabhu [14]).

4. Stationary probabilities with reflecting barriers at 0 and a

We now consider the effect of the walls of a container on the movement of the particle. We suppose that at 0 and a there are reflecting barriers which here we assume are defined in the following way. If the particle is at 0 in path i, $i = 1, 2$, then at the next move it has probability $p_i + q_i$ of moving to the right, r_i of staying at 0 in path i, and s_i of staying at 0 but switching paths. Similarly, if the particle is at a in path i, then at the next move it has probability $p_i + q_i$ of moving to the left, r_i of remaining at a in path i, and s_i of remaining at a but in the other path. If we define

$$u_{-1,n} = v_{-1,n} = u_{a+1,n} = v_{a+1,n} = 0, \tag{4.1}$$

then, instead of (2.2), we have the forward equations for $0 \leqslant k \leqslant a$ and $n \geqslant 0$:

$$\left.\begin{aligned} u_{k,n+1} &= p_1 u_{k-1,n} + r_1 u_{k,n} + q_1 u_{k+1,n} + s_2 v_{k,n} + p_1 u_{a,n} \delta_{k\,a-1} + q_1 u_{0,n} \delta_{k1} \\ &\text{and} \\ v_{k,n+1} &= p_2 v_{k-1,n} + r_2 v_{k,n} + q_2 v_{k+1,n} + s_1 u_{k,n} + p_2 v_{a,n} \delta_{k\,a-1} + q_2 v_{0,n} \delta_{k1}, \end{aligned}\right\} \tag{4.2}$$

where again δ_{ij} is the usual Kronecker delta. If we introduce generating functions

$$U_n(z) = \sum_{k=0}^{a} u_{k,n} z^k \quad \text{and} \quad V_n(z) = \sum_{k=0}^{a} v_{k,n} z^k, \tag{4.3}$$

and if initially the particle is at 0 in path 1 with probability u_0 and in path 2 with probability v_0 where $u_0 + v_0 = 1$, then we have

$$U_0(z) = u_0 \quad \text{and} \quad V_0(z) = v_0. \tag{4.4}$$

From (4.2) and (4.3) we obtain

$$\left.\begin{aligned} U_{n+1}(z) &= (p_1 z + r_1 + q_1 z^{-1}) U_n(z) + s_2 V_n(z) - (z - z^{-1})(p_1 u_{a,n} z^a - q_1 u_{0,n}) \\ &\text{and} \\ V_{n+1}(z) &= (p_2 z + r_2 + q_2 z^{-1}) V_n(z) + s_1 U_n(z) - (z - z^{-1})(p_2 v_{a,n} z^a - q_2 v_{0,n}). \end{aligned}\right\} \tag{4.5}$$

If we introduce generating functions similar to those defined by (2.8), then from (4.5) we see that the resulting expressions are equally intractable as those given by (2.9). Instead we make use of (4.5) to deduce the stationary ($n \to \infty$) probabilities.

We let π_k and ϕ_k denote the stationary probabilities that the particle is at k in paths 1 or 2, respectively. We define

$$\Pi(z) = \sum_{k=0}^{a} \pi_k z^k \quad \text{and} \quad \Phi(z) = \sum_{k=0}^{a} \phi_k z^k, \tag{4.6}$$

and from (4.5) we can deduce that

$$\left.\begin{aligned} \Pi(z) &= \frac{(1+z)}{\Delta(z)}\{[(1-z)(p_2 z - q_2) + s_2 z](p_1 \pi_a z^a - q_1 \pi_0) \\ &\qquad\qquad + s_2 z(p_2 \phi_a z^a - q_2 \phi_0)\} \\ \text{and} \qquad & \\ \Phi(z) &= \frac{(1+z)}{\Delta(z)}\{[(1-z)(p_1 z - q_1) + s_1 z](p_2 \phi_a z^a - q_2 \phi_0) \\ &\qquad\qquad + s_1 z(p_1 \pi_a z^a - q_1 \pi_0)\}, \end{aligned}\right\} \tag{4.7}$$

where $\Delta(z)$ is defined by

$$\Delta(z) = (1-z)(p_1 z - q_1)(p_2 z - q_2) + s_1 z(p_2 z - q_2) + s_2 z(p_1 z - q_1). \tag{4.8}$$

Assuming that p_i and q_i, $i = 1, 2$, are nonzero, the four constants π_0, ϕ_0, π_a and ϕ_a are determined by requiring that $\Pi(z)$ and $\Phi(z)$ are analytic at the three roots of the cubic $\Delta(z) = 0$, namely

$$\begin{aligned} &p_1 p_2 z^3 - (q_1 p_2 + q_2 p_1 + s_1 p_2 + s_2 p_1 + p_1 p_2) z^2 \\ &\qquad + (q_1 p_2 + q_2 p_1 + s_1 q_2 + s_2 q_1 + q_1 q_2) z - q_1 q_2 = 0, \end{aligned} \tag{4.9}$$

together with the normalizing condition

$$\Pi(1) + \Phi(1) = 1. \tag{4.10}$$

From the condition that the numerators in (4.7) should vanish at the roots z_j, $j = 1, 2, 3$, of (4.9) we can deduce, for $j = 1, 2, 3$,

$$p_1 p_2(s_1 \pi_a - s_2 \phi_a) z_j^{a+1} - (s_1 p_1 q_2 \pi_a - s_2 p_2 q_1 \phi_a) z_j^a + q_1 q_2(s_1 \pi_0 - s_2 \phi_0) = 0. \tag{4.11}$$

Clearly, with p_i and q_i, $i = 1, 2$, nonzero, a limiting distribution exists if and only if

$$\begin{vmatrix} z_1^{a+1} & z_1^a & 1 \\ z_2^{a+1} & z_2^a & 1 \\ z_3^{a+1} & z_3^a & 1 \end{vmatrix} = 0. \tag{4.12}$$

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Thus, in general, the condition for a stationary distribution to exist is non-trivial and we shall not discuss (4.12) further. For purposes of illustration we consider the case when the probabilities p_i and q_i, $i = 1, 2$, satisfy the condition

$$p_1 q_2 = p_2 q_1, \tag{4.13}$$

which we note includes the important special case of a free particle $p_i = q_i$, $i = 1, 2$.

Assuming that (4.13) holds we see that (4.11) becomes, for $j = 1, 2, 3$,

$$(s_1 \pi_a - s_2 \phi_a) z_j^a (z_j - \lambda) + \lambda^2 (s_1 \pi_0 - s_2 \phi_0) = 0, \tag{4.14}$$

where $\lambda = q_1/p_1 = q_2/p_2$. Now, in this case, one root of (4.9) is λ and therefore from (4.14) we have

$$s_1 \pi_0 = s_2 \phi_0 \quad \text{and} \quad s_1 \pi_a = s_2 \phi_a. \tag{4.15}$$

From (4.7), (4.8), (4.13) and (4.15) we deduce that

$$\Pi(z) = (1+z)(z-\lambda)^{-1}(\pi_a z^a - \lambda \pi_0) \quad \text{and} \quad \Phi(z) = (1+z)(z-\lambda)^{-1}(\phi_a z^a - \lambda \phi_0). \tag{4.16}$$

Now, clearly, we require

$$\pi_0 = \lambda^{a-1} \pi_a \quad \text{and} \quad \phi_0 = \lambda^{a-1} \phi_a, \tag{4.17}$$

and, making use of (4.10), we finally obtain

$$\left.\begin{aligned} \Pi(z) &= \frac{\lambda^{a-1}(1-\lambda) f_2}{2(1-\lambda^a)} (1+z) \left\{ \frac{1-(z/\lambda)^a}{1-(z/\lambda)} \right\} \\ \text{and} \qquad & \\ \Phi(z) &= \frac{\lambda^{a-1}(1-\lambda) f_1}{2(1-\lambda^a)} (1+z) \left\{ \frac{1-(z/\lambda)^a}{1-(z/\lambda)} \right\}, \end{aligned}\right\} \tag{4.18}$$

where f_1 and f_2 are defined by $(3.1)_3$. Thus, for example, we have

$$\left.\begin{aligned} \pi_k &= \frac{f_2(1-\lambda^2)}{2(1-\lambda^a)} \lambda^{a-1-k}, \quad 1 \leqslant k \leqslant a-1, \\ \pi_0 &= \frac{f_2(1-\lambda)}{2(1-\lambda^a)} \lambda^{a-1} \quad \text{and} \quad \pi_a = \frac{f_2(1-\lambda)}{2(1-\lambda^a)}, \end{aligned}\right\} \tag{4.19}$$

and similarly for ϕ_k. We notice that in the free particle case, $\lambda = 1$, we have

$$\pi_k = \frac{f_2}{a}, \quad 1 \leqslant k \leqslant a-1 \quad \text{and} \quad \pi_0 = \pi_a = \frac{f_2}{2a}. \tag{4.20}$$

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5. Absorption at 0 with absorbing barriers at 0 and a

In this section we determine the probabilities of ultimate absorption at 0 from the position k given that 0 and a are absorbing barriers. Physically the problem corresponds to obtaining the probability of particle escape at 0 from position k in an open ended container. We let ψ_k and ω_k be the probabilities of absorption at 0 from position k in paths 1 and 2, respectively. For $1 \leqslant k \leqslant a-1$ we have the backward equations

$$\left.\begin{aligned} \psi_k &= p_1\psi_{k+1}+q_1\psi_{k-1}+r_1\psi_k+s_1\omega_k \\ \text{and}\qquad \omega_k &= p_2\omega_{k+1}+q_2\omega_{k-1}+r_2\omega_k+s_2\psi_k, \end{aligned}\right\} \tag{5.1}$$

and clearly we have in addition

$$\psi_0 = \omega_0 = 1 \quad \text{and} \quad \psi_a = \omega_a = 0. \tag{5.2}$$

To solve these equations we introduce generating functions

$$\Psi(z) = \sum_{k=1}^{a-1} \psi_k z^k \quad \text{and} \quad \Omega(z) = \sum_{k=1}^{a-1} \omega_k z^k, \tag{5.3}$$

and in the usual way from (5.1) and (5.2) we obtain

$$\left.\begin{aligned} \Psi(z) &= \frac{z}{\Theta(z)}\{[(1-z)(q_2 z-p_2)+s_2 z][-p_1\psi_1+q_1(z-\psi_{a-1}z^a)] \\ &\qquad +s_1 z[-p_2\omega_1+q_2(z-\omega_{a-1}z^a)]\} \\ \text{and}\qquad & \\ \Omega(z) &= \frac{z}{\Theta(z)}\{[(1-z)(q_1 z-p_1)+s_1 z][-p_2\omega_1+q_2(z-\omega_{a-1}z^a)] \\ &\qquad +s_2 z[-p_1\psi_1+q_1(z-\psi_{a-1}z^a)]\}, \end{aligned}\right\} \tag{5.4}$$

where $\Theta(z)$ is defined by

$$\Theta(z) = (1-z)[(1-z)(q_1 z-p_1)(q_2 z-p_2)+s_1 z(q_2 z-p_2)+s_2 z(q_1 z-p_1)]. \tag{5.5}$$

Again assuming that p_i and q_i, $i = 1, 2$, are nonzero, we determine the four constants $\psi_1, \omega_1, \psi_{a-1}$ and ω_{a-2} by requiring that $\Psi(z)$ and $\Omega(z)$ are analytic at the four roots of $\Theta(z) = 0$. One root is clearly $z = 1$, while the others are roots of a cubic. Thus the determination of the absorption probabilities involves solving a four by four nonhomogeneous system of equations. In general this is a nontrivial problem and we shall only give explicit expressions for absorption probabilities for the special case when (4.13) is satisfied.

With λ as defined previously we have that in this special case one root of the cubic is λ^{-1} and, from the condition that the numerators of (5.4) vanish for the other two roots of the cubic, we can deduce

$$\psi_1 = \omega_1 \quad \text{and} \quad \psi_{a-1} = \omega_{a-1}. \tag{5.6}$$

On requiring that the numerators of (5.4) also vanish for $z = 1$ we obtain

$$\psi_1 = \lambda(1 - \psi_{a-1}). \tag{5.7}$$

Using (5.6) and (5.7) in (5.4) and (5.5) we obtain

$$\Psi(z) = \Omega(z) = \frac{\lambda[\psi_{a-1}(1-z^a)-(1-z)]}{(1-z)(\lambda - z^{-1})}. \tag{5.8}$$

However, these generating functions are analytic at $z = \lambda^{-1}$ and thus we have

$$\psi_{a-1} = \lambda^{a-1}(1-\lambda)(1-\lambda^a)^{-1}. \tag{5.9}$$

From (5.9) we can simplify (5.8) to read

$$\Psi(z) = \Omega(z) = \lambda z\left\{\frac{1-(\lambda z)^a}{1-(\lambda z)}\right\} - \lambda^a z\left\{\frac{1-z^a}{1-z}\right\}, \tag{5.10}$$

from which the required probabilities are immediate, namely

$$\psi_k = \omega_k = (\lambda^k - \lambda^a)(1-\lambda^a)^{-1}. \tag{5.11}$$

We observe that in the special case of $\lambda = 1$ we have simply

$$\psi_k = \omega_k = 1 - ka^{-1}. \tag{5.12}$$

6. Continuous model for a medium with two distinct diffusion paths

In this section we show that the continuous version of the model given in Section 2 gives rise to the coupled system of partial differential equations (1.2) in the special case of $p_i = q_i$, $i = 1, 2$. We suppose that each step has length Δx and that the time between consecutive steps is Δt. Formally, we replace k and n by x and t, respectively, and we introduce functions $f(x,t)$ and $g(x,t)$ such that in the limit of Δx and Δt tending to zero, $u_{k,n}$ and $v_{k,n}$ are approximately $f(x,t)\,dx$ and $g(x,t)\,dx$, respectively. The equations corresponding to (2.2) are

$$\left.\begin{aligned} &f(x,t+\Delta t) = p_1 f(x-\Delta x,t) + r_1 f(x,t) + q_1 f(x+\Delta x,t) + s_2\, g(x,t) \\ \text{and}\quad & \\ &g(x,t+\Delta t) = p_2\, g(x-\Delta x,t) + r_2\, g(x,t) + q_2\, g(x+\Delta x,t) + s_1 f(x,t). \end{aligned}\right\} \tag{6.1}$$

Up to first order in Δt and second order in Δx (6.1) becomes

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$$\left.\begin{aligned}\Delta t\frac{\partial f}{\partial t} &= \frac{(p_1+q_1)}{2}(\Delta x)^2\frac{\partial^2 f}{\partial x^2}-(p_1-q_1)\Delta x\frac{\partial f}{\partial x}-s_1 f+s_2 g \\ \text{and} \qquad \Delta t\frac{\partial g}{\partial t} &= \frac{(p_2+q_2)}{2}(\Delta x)^2\frac{\partial^2 g}{\partial x^2}-(p_2-q_2)\Delta x\frac{\partial g}{\partial x}-s_2 g+s_1 f,\end{aligned}\right\} \tag{6.2}$$

where we have made use of (2.1). We now suppose Δt and Δx tend to zero in such a way that $\Delta t/(\Delta x)^2$ tends to a finite positive limit λ^*. Further, we assume that the various probabilities p_i, q_i and s_i, $i = 1,2$, are such that

$$p_i = \lambda^*(D_i+d_i\,\Delta x), \quad q_i = \lambda^*(D_i-d_i\,\Delta x) \quad \text{and} \quad s_i = \lambda^* k_i(\Delta x)^2, \tag{6.3}$$

where d_i, D_i and k_i, $i = 1,2$, are assumed to be finite constants. Clearly, from (6.2) and (6.3) we obtain

$$\left.\begin{aligned}\frac{\partial f}{\partial t} &= D_1\frac{\partial^2 f}{\partial x^2}-2d_1\frac{\partial f}{\partial x}-k_1 f+k_2 g \\ \text{and} \qquad \frac{\partial g}{\partial t} &= D_2\frac{\partial^2 g}{\partial x^2}-2d_2\frac{\partial g}{\partial x}-k_2 g+k_1 f.\end{aligned}\right\} \tag{6.4}$$

In the case of a free particle, $p_i = q_i$, $i = 1,2$, we obtain (1.2) and we observe that the constants k_1 and k_2 are essentially transition probabilities. Thus the inequalities (1.3) are immediate.

In Aifantis and Hill [4] asymptotic formulae are given for the source solutions of (1.2), that is for solutions of (1.2) with initial conditions

$$c_1(x,0) = c_1^0\,\delta(x) \quad \text{and} \quad c_2(x,0) = c_2^0\,\delta(x), \tag{6.5}$$

where c_1^0 and c_2^0 are constants specifying the strength of the source, and $\delta(x)$ denotes the usual Dirac delta function. For small times it is shown that

$$c_1(x,t) = c_1^0\frac{e^{-x^2/4D_1 t}}{(4\pi D_1\,t)^{\frac{1}{2}}}+O(t^{\frac{1}{2}}) \quad \text{and} \quad c_2(x,t) = c_2^0\frac{e^{-x^2/4D_2 t}}{(4\pi D_2\,t)^{\frac{1}{2}}}+O(t^{\frac{1}{2}}), \tag{6.6}$$

for $-\infty < x < \infty$. For large times the total concentraton c_1+c_2 is given by

$$c_1(x,t)+c_2(x,t) = (c_1^0+c_2^0)\frac{e^{-x^2/4D^* t}}{(4\pi D^*\,t)^{\frac{1}{2}}}+O(t^{-3/2}), \tag{6.7}$$

for $-\infty < x < \infty$, where D^* is given by

$$D^* = \left\{\frac{D_1 k_2+D_2 k_1}{k_1+k_2}\right\}. \tag{6.8}$$

Thus, for small times, both c_1 and c_2 follow the classical solution but with diffusivities D_1 and D_2, respectively, while for large times the total concentration

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follows the classical solution with diffusivity D^*. This problem is analogous to the unrestricted random walk considered in Sections 2 and 3. By applying the central limit theorem twice we can deduce an asymptotic formula for the total concentration which confirms (6.7) but, more importantly, demonstrates the deviations of c_1+c_2 from the classical formula.

In order to utilize the formulae of Section 3 for the source solutions we need to rescale $c_1(x,t)$ and $c_2(x,t)$ by dividing by $c_1^0+c_2^0$ so that we can identify u_0 and v_0 with $c_1^0/(c_1^0+c_2^0)$ and $c_2^0/(c_1^0+c_2^0)$, respectively. Thus we identify $f(x,t)$ and $g(x,t)$ with $c_1(x,t)/(c_1^0+c_2^0)$ and $c_2(x,t)/(c_1^0+c_2^0)$, respectively. Now $f(x,t)+g(x,t)$ is a well-defined probability density function for the position of the particle at time t. If the mean and variance of the position of the particle are denoted by $\mu(t)$ and $\sigma(t)^2$, respectively, then, as $t\to\infty, f+g$ is asymptotically normally distributed with mean $\mu(t)$ and variance $\sigma(t)^2$. If we consider the case of $p_i=q_i, i=1,2$, then $\mu(t)=0$ and we have therefore

$$f(x,t)+g(x,t)\sim\frac{e^{-x^2/2\sigma(t)^2}}{\sqrt{(2\pi)}\,\sigma(t)}\quad\text{as } t\to\infty. \tag{6.9}$$

Now we can deduce an expression for the variance $\sigma(t)^2$ from (3.17). We have $\sigma(t)^2=\sigma_n^2(\Delta x)^2$ and, from (6.3) and $\Delta t=\lambda^*(\Delta x)^2$, we obtain from (3.17)

$$\sigma(t)^2=2D^*t+\frac{2}{(k_1+k_2)}\left\{\frac{(D_1c_1^0+D_2c_2^0)}{(c_1^0+c_2^0)}-D^*\right\}[1-e^{-(k_1+k_2)t}], \tag{6.10}$$

where D^* is given by (6.8) and, in deriving (6.10), we formally replaced n by $t/\Delta t$. Thus, in summary, the asymptotic form for the total concentration becomes

$$c_1(x,t)+c_2(x,t)\sim\frac{(c_1^0+c_2^0)\,e^{-x^2/2\sigma(t)^2}}{\sqrt{(2\pi)}\,\sigma(t)}\quad\text{as } t\to\infty, \tag{6.11}$$

where the variance $\sigma(t)^2$ is given by (6.10). We observe that (6.7) and (6.11) are consistent since as, $t\to\infty$, the first term of the right-hand side of (6.10) dominates and the variance in (6.11) is merely $2D^*t$, which is in agreement with (6.7). Table 1 gives numerical values of c_1+c_2 as given by (6.11) and (6.7) and divided by the exact value of c_1+c_2 obtained from Aifantis and Hill [4]. Clearly (6.11) provides a useful approximation to the total concentration. It is closer than (6.7) to the exact value for smaller values of t while for larger values of t (6.7) is marginally more accurate. The asterisk (*) indicates the better approximation.

It is difficult to relate (6.11) as an approximate formulae to the exact expression given by Aifantis and Hill [4]. However, some analytic insight can be obtained by recalling that both c_1 and c_2, and therefore the total concentration, satisfy

$$\frac{\partial^2 c}{\partial t^2}+(k_1+k_2)\frac{\partial c}{\partial t}=(k_1D_2+k_2D_1)\nabla^2c+(D_1+D_2)\frac{\partial}{\partial t}\nabla^2c-D_1D_2\nabla^4c, \tag{6.12}$$

TABLE 1

Comparison of $c_1 + c_2$ as given by (6.11) and (6.7) for $D_1 = k_1 = c_1^0 = 2$, $D_2 = k_2 = c_2^0 = 1$ and $x = 2$

t	(6.11)/(exact)	(6.7)/(exact)
0·5	1·0532*	0·9425
1·5	1·0095*	1·0102
2·5	1·0006*	1·0074
3·5	0·9983*	1·0051
4·5	0·9977*	1·0038
5·5	0·9975*	1·0030
6·5	0·9975	1·0024*
7·5	0·9976	1·0020*
8·5	0·9977	1·0017*
9·5	0·9978	1·0015*

which is obtained by eliminating either of c_1 or c_2 from (1.2). If now we look for a solution of the form

$$c(\mathbf{x}, t) = h(\mathbf{x}, \tau) \quad \text{and} \quad \tau = \sigma(t)^2/2, \tag{6.13}$$

where $h(\mathbf{x}, \tau)$ is assumed to satisfy the classical diffusion equation (1.1) with t replaced by τ, and unit diffusivity, then (6.12) becomes

$$\begin{aligned} &\frac{\partial^2 h}{\partial \tau^2}\{(\sigma\sigma' - D_1)(\sigma\sigma' - D_2)\} \\ &\quad + \frac{\partial h}{\partial \tau}\{\sigma\sigma'' + \sigma'^2 + (k_1 + k_2)\sigma\sigma' - (k_1 D_2 + k_2 D_1)\} = 0, \end{aligned} \tag{6.14}$$

where primes denote derivatives with respect to t. In the particular case of interest with $h(x, t)$ as the classical source solution we have

$$\frac{\partial h}{\partial \tau} = \frac{h}{\sigma^2}\left\{\left(\frac{x}{\sigma}\right)^2 - 1\right\} \quad \text{and} \quad \frac{\partial^2 h}{\partial \tau^2} = \frac{h}{\sigma^4}\left\{\left(\frac{x}{\sigma}\right)^4 - 6\left(\frac{x}{\sigma}\right)^2 + 3\right\}. \tag{6.15}$$

If we assume the variance $\sigma(t)^2$ is vanishingly small for small times and tends to infinity with t then, from (6.14) and (6.15), we observe that for t small the first term of (6.14) dominates so that

$$\sigma(t)^2 = 2D_1 t \quad \text{or} \quad \sigma(t)^2 = 2D_2 t. \tag{6.16}$$

which can be reconciled with (6.6). Alternatively, for large t we see from (6.14) and (6.15) that the second term in (6.14) is the dominant expression and therefore we have

$$\sigma\sigma'' + \sigma'^2 + (k_1 + k_2)\sigma\sigma' = (k_1 D_2 + k_2 D_1). \tag{6.17}$$

On integrating this equation we obtain

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$$\sigma(t)^2 = 2D^* t + A^* + B^* e^{-(k_1+k_2)t}, \tag{6.18}$$

where D^* is given by (6.8) and A^* and B^* are constants of integration. If we require that the variance is zero at $t = 0$ then (6.18) becomes

$$\sigma(t)^2 = 2D^* t + A^*[1 - e^{-(k_1+k_2)t}]. \tag{6.19}$$

Thus we can provide a fairly plausible independent derivation of the general form of the expression (6.10) for $\sigma(t)^2$. However, it is difficult to see how one might identify the constant A^* in (6.19) other than by the calcuations given in Section 3.

Finally in this section we note the equations corresponding to (6.4) for the case of n diffusion paths. We let s_{ij}, $i,j = 1,2,\ldots,n$, denote the transition probabilities from path i to path j. We have

$$p_i + q_i + r_i + \sum_{\substack{j=1 \\ j \neq i}}^{n} s_{ij} = 1, \quad i = 1,2,\ldots,n, \tag{6.20}$$

and we assume that p_i and q_i are given by (6.3) and that

$$s_{ij} = \lambda^* k_{ij}(\Delta x)^2. \tag{6.21}$$

If $f_i(x,t)$ denotes the probability density function for the position of the particle in path i then, instead of (6.4), we can show that we have

$$\frac{\partial f_i}{\partial t} = D_i \frac{\partial^2 f_i}{\partial x^2} - 2d_i \frac{\partial f_i}{\partial x} - \left(\sum_{\substack{j=1 \\ j \neq i}}^{n} k_{ij} \right) f_i + \sum_{\substack{j=1 \\ j \neq i}}^{n} k_{ji} f_j, \tag{6.22}$$

for $i = 1,2,\ldots,n$. For the case of the free particle these equations have been given by Aifantis [2] without specifying the signs of the various coefficients in (6.22). They are clearly apparent from this formulation since $k_{ij} \geqslant 0$.

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References

[1] E. C. Aifantis, "Introducing a multiporous medium", *Developments in mechanics, Proc. 15th Midwestern Mech, Conf.* 8 (1977), 209–211.

[2] E. C. Aifantis, "A new interpretation of diffusion in high-diffusivity paths—a continuum approach", *Acta Metall.* 27, (1979), 683–691.

[3] E. C. Aifantis, "Continuum basis for diffusion in regions with multiple diffusivity", *J. Appl. Phys.* 50 (1979), 1334–1338.

[4] E. C. Aifantis and J. M. Hill, "On the theory of diffusion in media with double diffusivity. Part I. Basic mathematical results", *Quart. J. Mech. Appl. Math.* 33 (1980).

[5] G. I. Barenblatt, Iu. P. Zheltov and I. N. Kochina, "Basic concepts in the theory of seepage of homogenous liquids in fissured rocks [strata]", *J. Appl. Math. Mech.* 24 (1960), 1286–1303.
[6] V. D. Barnett, "A simple random walk on parallel axes moving at different rates", *J. Appl. Prob.* 12 (1975), 466–476.
[7] J. Crank, *Mathematics of diffusion* (Oxford University Press, 2nd edition, 1967).
[8] S. D. Eidelman, *Parabolic systems* (North-Holland Pub. Co. Amsterdam, 1969).
[9] W. Feller, *An introduction to probability theory and its applications*, Vol. 2 (Wiley, 1966).
[10] A. Friedman, *Partial differential equations of parabolic type* (Prentice-Hall, 1964).
[11] H. L. Frisch and J. M. Hammersley, "Percolation processes and related topics", *J. Soc. Indust. Appl. Math.* 11 (1963), 894–918.
[12] J. M. Hill and E. C. Aifantis, "On the theory of diffusion in media with double diffusivity. Part II. Boundary value problems", *Quart. J. Mech. Appl. Math.* 33 (1980).
[13] A. McNabb, "Comparison and existence theorems for multicomponent diffusion systems", *J. Math. Anal. Applics.* 3 (1961), 133–144.
[14] N. U. Prabhu, *Stochastic processes* (Macmillan, 1966).
[15] J. Szarski, *Differential inequalities* (PWN, Warsaw, 1968).

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