Continuum and random-walk models of magnetic relaxation in porous media

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Nuclear magnetic relaxation in porous media can be treated by a continuum model, involving the solution of an initial boundary-value problem, or by a random-walk model, involving a random walk on a lattice with a partially absorbing boundary. Three formulations of the random-walk model have appeared in the literature. These have different step probabilities and different relations between the parameters of the random walk and continuum models. This paper reexamines the formulation presented previously by the author. That formulation is revised to improve the approximation to the continuum model and to simplify comparison with the other formulations. It is shown that the three formulations are largely the same but represent two different orders of approximation to the continuum model and retain some differences that are difficult to understand.

Two models, a continuum and a random-walk model, have been used to investigate nuclear magnetic relaxation in porous media. There has been some disagreement in the literature[1–3] about the correct way to formulate the random-walk model and the relation of its parameters to those of the continuum model. In this paper I reexamine the random-walk formulation that I presented earlier.[2] That formulation is revised to improve the approximation to the continuum model and to simplify comparison with the other formulations. The three random-walk formulations are largely the same. However, they represent two different orders of approximation to the continuum model. And they retain some differences that are difficult to understand.

The discussion in this paper will be limited to a one-dimensional pore of length a.[4] In the continuum model, the magnetization M of the pore fluid satisfies the diffusion equation

$$\frac{\partial M}{\partial t} = D\frac{\partial^2 M}{\partial x^2}, \tag{1}$$

where D is the bulk self-diffusion coefficient of the pore fluid. In Eq. (1) I have neglected bulk relaxation. This could easily be included if desired, but is not important for the present discussion. At the boundary $x = 0$, M satisfies the condition

$$-D\frac{\partial M}{\partial x} + \rho M = 0, \tag{2}$$

where ρ is a surface relaxation velocity. There is a similar boundary condition at $x = a$. Finally, M satisfies the initial condition

$$M(x,0) = M_0. \tag{3}$$

In the random-walk model, walkers start with equal probability from any point in the pore space. When a walker attempts to step out of the pore space into the matrix it has a probability of being killed. The magnetization is related to $g(x,t)$, the average number of walkers still alive at point x at time t, by

$$M(x,t) = M_0 g(x,t). \tag{4}$$

The number of walkers is normalized to $g(x,0) = 1$.

Let us begin by reviewing the formulation of the random walk presented in Ref. 2. We divide the pore into cells of length ϵ and place a lattice site at the center of each cell. The lattice sites are spaced a distance ϵ apart. The lattice sites in the boundary cells are located at the positions $x = \epsilon/2$ and $x = a - \epsilon/2$.

A random walker is placed on the lattice with equal probability to be placed on any lattice site. The walker takes steps at equal intervals of time τ_s.[5] At each step the walker chooses a direction with probability 1/2. If the walker is at an interior site of the lattice it steps to the neighboring site in that direction with probability μ, remaining at its initial site with probability $1 - \mu$. If the walker is at a boundary site and it has chosen the direction to the interior, it steps to the neighboring site with probability μ. If it has chosen the direction to the wall, it steps there and is killed with probability γ. And it remains at the boundary site with probability $1 - (\mu + \gamma)/2$.

We evaluate the change of the number $g(x,t)$ at each step by considering all transitions to and from the site x. This yields for an interior point

$$\frac{g(x,t+\tau_s) - g(x,t)}{\tau_s} = \frac{\mu\epsilon^2}{2\tau_s}\frac{g(x+\epsilon,t) - 2g(x,t) + g(x-\epsilon,t)}{\epsilon^2}. \tag{5}$$

For the boundary site $x = \epsilon/2$ it yields

$$-\epsilon\frac{g(\epsilon/2,t+\tau_s) - g(\epsilon/2,t)}{\tau_s} = -\frac{\mu\epsilon^2}{2\tau_s}\frac{g(3\epsilon/2,t) - g(\epsilon/2,t)}{\epsilon} + \frac{\gamma\epsilon}{2\tau_s}g(\epsilon/2,t). \tag{6}$$

There is a similar equation for the site $x = a - \epsilon/2$. If we now make the association[6]

$$D = \mu\epsilon^2/2\tau_s \tag{7}$$

and

$$\rho = \gamma\epsilon/2\tau_s, \tag{8}$$

then Eqs. (5) and (6) reduce to Eqs. (1) and (2) in the limit $\epsilon \to 0, \tau_s \to 0, \gamma \to 0$.

Dividing Eq. (8) by Eq. (7) gives

$$\delta \equiv \rho\epsilon/D = \gamma/\mu. \tag{9}$$

Clearly values of γ and μ, each between 0 and 1, can be chosen to satisfy this equation for any value of δ. Once γ and μ have been chosen, τ_s can always be chosen to satisfy Eqs. (7) and (8). Thus, contrary to a comment of Wilkinson, Johnson, and Schwartz (Ref. 22 in Ref. 3), this formulation can be applied for any values of ρ and D.

The discussion above is the formulation of the random walk given in Ref. 2. In this formulation, Eq. (5), with Eq. (7), approximates Eq. (1) to $O(\epsilon^2)$ (Ref. 7) but Eq. (6), with Eqs. (7) and (8), approximates Eq. (2) only to $O(\epsilon)$. To get a better approximation to the boundary condition we introduce[7] the fictitious site $x = -\epsilon/2$. A Taylor's series expansion around the point $x = 0$ yields

$$g(\pm\epsilon/2, t) = g(0, t) \pm \frac{\epsilon}{2}\left.\frac{\partial g}{\partial x}\right|_{x=0} + \frac{\epsilon^2}{8}\left.\frac{\partial^2 g}{\partial x^2}\right|_{x=0} + \cdots. \tag{10}$$

From Eq. (10) we have immediately

$$g(0, t) = \frac{g(\epsilon/2, t) + g(-\epsilon/2, t)}{2} + O(\epsilon^2) \tag{11}$$

and

$$\left.\frac{\partial g}{\partial x}\right|_{x=0} = \frac{g(\epsilon/2, t) - g(-\epsilon/2, t)}{\epsilon} + O(\epsilon^2). \tag{12}$$

Substituting Eqs. (11) and (12) into Eq. (2) then gives the boundary condition

$$-D\frac{g(\epsilon/2, t) - g(-\epsilon/2, t)}{\epsilon} + \rho\frac{g(\epsilon/2, t) + g(-\epsilon/2, t)}{2} = 0 \tag{13}$$

correct to $O(\epsilon^2)$.

Keeping Eq. (7), we now apply Eq. (5) to the point $x = \epsilon/2$ and eliminate $g(-\epsilon/2, t)$ between this equation and Eq. (13). This yields Eq. (6) but, instead of Eqs. (8) or (9), we now have

$$\frac{\gamma}{\mu} = \frac{2\delta}{2 + \delta}, \tag{14}$$

which gives the boundary condition correct to $O(\epsilon^2)$.

This formulation of the random-walk problem is conceptually straightforward and convenient to program for computing. However, for small μ the walker spends most of the time standing still so this formulation can be very uneconomical of computer time. We can reformulate the random walk in a way that is equivalent but more economical. For a walker at an interior lattice site we calculate the probability p that its first move is to the right and the average time τ before it moves. These quantities are given by

$$p = \frac{\mu}{2}\sum_{n=0}^{\infty}(1 - \mu)^n = \tfrac{1}{2} \tag{15}$$

and

$$\tau = \mu\tau_s\sum_{n=0}^{\infty}(n + 1)(1 - \mu)^n = \frac{\tau_s}{\mu}. \tag{16}$$

From symmetry the probability and average time for a move to the left are the same.

For a walker on a boundary site, directions to the right and left are not symmetric. We must calculate the probability P_d that the walker first moves to the wall and is killed, the average time Δt_d for this to occur, the probability P_e that the walker first moves to the neighboring interior site, and the average time Δt_e for this to occur. The quantities P_d and Δt_d are given by

$$P_d = \frac{\gamma}{2}\sum_{n=0}^{\infty}\left(1 - \frac{\mu + \gamma}{2}\right)^n = \frac{\gamma}{\mu + \gamma} \tag{17}$$

and

$$\Delta t_d = \frac{\gamma\tau_s}{2P_d}\sum_{n=0}^{\infty}(n + 1)\left(1 - \frac{\mu + \gamma}{2}\right)^n = \frac{2\mu\tau}{\mu + \gamma}. \tag{18}$$

The quantities P_e and Δt_e are given by similar expressions but with γ and P_d, in the factors to the left of the summation signs, replaced respectively by μ and P_e. This gives $P_e = 1 - P_d$ and $\Delta t_e = \Delta t_d$. Substituting Eq. (9) into Eqs. (17) and (18) gives

$$P_d = \frac{\delta}{1 + \delta} \tag{19}$$

and

$$\Delta t_d = \frac{2\tau}{1 + \delta} \tag{20}$$

for the $O(\epsilon)$ approximation. Substituting Eq. (14) into Eqs. (17) and (18) gives

$$P_d = \frac{2\delta}{2 + 3\delta} \tag{21}$$

and

$$\Delta t_d = \frac{2\tau(2 + \delta)}{2 + 3\delta} \tag{22}$$

for the $O(\epsilon^2)$ approximation.

To complete the reformulation of the problem we substitute τ from Eq. (16) into Eq. (7) to obtain

$$D = \epsilon^2/2\tau. \tag{23}$$

In the reformulated walk, a walker at an interior lattice site steps to the right or left with probability 1/2. At each step the clock is advanced by an amount τ. A walker at a boundary site steps to the neighboring interior site with probability P_e. In this case the clock is advanced by an

amount Δt_e. The walker steps to the wall and is killed with probability P_d and the clock is then advanced by an amount Δt_d.

The reformulated random walk can be set up directly without using the argument based on the original form of the random walk discussed here. To see this we determine the rate of change of $g(x,t)$ by considering the rates of jumps to and away from the site x. Then for the interior sites that are not neighbors to boundary sites we obtain

$$\frac{\partial g(x,t)}{\partial t} = \frac{1}{2\tau}[g(x+\epsilon,t) - 2g(x,t) + g(x-\epsilon,t)]. \quad (24)$$

For the sites near $x = 0$ we obtain

$$\frac{\partial g(3\epsilon/2,t)}{\partial t} = \frac{1}{2\tau}[g(5\epsilon/2,t) - 2g(3\epsilon/2,t)] + \frac{P_e}{\Delta t_e} g(\epsilon/2,t) \quad (25)$$

and

$$\frac{\partial g(\epsilon/2,t)}{\partial t} = \frac{1}{2\tau} g(3\epsilon/2,t) - \frac{P_e}{\Delta t_e} g(\epsilon/2,t) - \frac{P_d}{\Delta t_d} g(\epsilon/2,t) \quad (26)$$

with similar equations for the sites near $x = a$. These equations reduce to Eqs. (1) and (2) in the limit $\epsilon \to 0$ provided

$$\lim_{\epsilon\to 0} \frac{P_e \epsilon^2}{\Delta t_e} = \frac{\epsilon^2}{2\tau} = D \quad (27)$$

and

$$\lim_{\epsilon\to 0} \epsilon \left[\frac{P_d}{\Delta t_d} + \frac{P_e}{\Delta t_e} - \frac{1}{2\tau}\right] = \rho. \quad (28)$$

These conditions are satisfied by the values obtained above for both the $O(\epsilon)$ and $O(\epsilon^2)$ approximations.

We can now compare the reformulated random-walk problem with the formulations of Banavar and Schwartz[1] (pp. 284–287) and of Wilkinson, Johnson, and Schwartz.[3] For a walker on an interior site of the lattice the three formulations are identical. The walker steps to the right or left with probability 1/2. At each step the clock is advanced by an amount τ (denoted Δt in Ref. 3) given by Eq. (23).[6]

For a walker at a boundary site, Banavar and Schwartz state, in the paragraph before their Eq. (3.3), that "...magnetization decays with probability γ (per unit time step τ)." They relate γ to ρ by their Eq. (3.4), which can be written

$$\delta = \gamma/(1-\gamma). \quad (29)$$

Now, if we choose $\mu = 1 - \gamma$, Eq. (9) becomes the same as Eq. (29). Substituting this equation into Eq. (19) then gives $P_d = \gamma$ which appears to be the sense of the statement quoted above.

To this extent, the formulation of Banavar and Schwartz is the same as the $O(\epsilon)$ formulation of this paper. However, substituting Eq. (29) into Eq. (20) gives $\Delta t_d = 2\tau(1-\gamma)$ which does not appear in Ref. 1. Rather, from the statement quoted above, it appears that Banavar and Schwartz used $\Delta t_d = \tau$, but this does not satisfy Eq. (28) so the random-walk equations do not reduce to the continuum equations in the limit $\epsilon \to 0$. Furthermore, Banavar and Schwartz do not specify P_e and Δt_e. More information is needed in order to clarify their analysis.

For the walker on a boundary site, Wilkinson, Johnson, and Schwartz solve Eq. (1) with the boundary condition (2), the additional boundary condition $g(3\epsilon/2,t) = 0$, and the initial condition $g(x,0) = \delta(x - \epsilon/2)$. They calculate $P_d, P_e, \Delta t_d$, and Δt_e from this solution. From their Eq. (B4a), $P_d = 2\delta/(2+3\delta)$ and $P_e = 1 - P_d$, the same as in the $O(\epsilon^2)$ formulation of this paper. Equation (B4b) of Wilkinson, Johnson, and Schwartz is

$$\Delta t_e = \frac{\epsilon^2}{3D}\frac{12 + 11\delta + 3\delta^2}{(2+\delta)(2+3\delta)}, \quad \Delta t_d = \frac{\epsilon^2}{24D}\frac{46 + 15\delta}{2 + 3\delta}. \quad (30)$$

These satisfy Eq. (27), but not Eq. (28).

This failure to satisfy Eq. (28) raises a very difficult question. Suppose one specifies a random walk by choosing a set of parameters $\tau, P_d, P_e, \Delta t_d$, and Δt_e. In the limit $\epsilon \to 0$ does this random walk reduce to the continuum diffusion problem specified by Eqs. (1) and (2)? Equations (23), (27), and (28) are sufficient conditions to ensure that this occurs. But, are they necessary conditions? If they are, then there must be an error in the formulation of Wilkinson, Johnson, and Schwartz. But it is very difficult to see where such an error might be located. If the conditions are not necessary, it should be possible to show that the formulation of Wilkinson, Johnson, and Schwartz reduces to the continuum problem in the limit. But, it is not at all clear how this might be done. It is beyond the scope of this paper to resolve this question.

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[1] J. R. Banavar and L. M. Schwartz, in *Molecular Dynamics in Restricted Geometries*, edited by J. Klafter and J. M. Drake (Wiley, New York, 1989), p. 273.

[2] K. S. Mendelson, Phys. Rev. B **41**, 562 (1990).

[3] D. J. Wilkinson, D. L. Johnson, and L. M. Schwartz, Phys. Rev. B **44**, 4960 (1991).

[4] The d-dimensional generalization of the interior equations, (5) and (24), and of the $O(\epsilon)$ approximation to the boundary conditions is straightforward for a boundary of arbitrary shape. However, except for a boundary in the shape of a hypercube, the generalization of the $O(\epsilon^2)$ boundary conditions is not straightforward.

[5] This was denoted τ in Ref. 2 but is not the same quantity as τ in Ref. 1. In this paper I will follow Ref. 1 in using τ and Ref. 3 in using the symbols $P_d, P_e, \Delta t_d$, and Δt_e.

[6] For a space of d dimensions, the factor 2 in the denominators of Eqs. (7), (8), and (23) must be replaced by $2d$. Reference 2 treats a space of d dimensions and Ref. 1 a space of three dimensions.

[7] R. Ghez, *A Primer of Diffusion Problems* (Wiley, New York, 1988), pp. 15–21.