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Predictions for pulsed-field-gradient NMR experiments of diffusion in fractal spaces*

By R. A. Damion and K. J. Packer
Department of Chemistry, University of Nottingham, University Park, Nottingham NG7 2RD, UK.

In this paper, theoretical predictions are made for pulsed-field-gradient NMR experiments of diffusion in fractal spaces. We obtain the general q-space behaviour of the NMR signal, which upon Fourier transformation, delivers the probability density for displacements. We also show that there exists a power law behaviour in the limits of large q or small displacements.

Introduction

Within the past few decades there has been much interest in the phenomenon of anomalous diffusion and, in particular, what has become known as fractional Brownian motion (Mandelbrot & Van Ness 1968; Gefen *et al.* 1983; Voss 1989; Metzler *et al.* 1994). Fractional Brownian motion is recognised by the characteristic dependence on time of, for example, the second moment of its increments:

$$< \mathbf{r}^2(t) > \sim t^{2H}, \tag{1}$$

where subdiffusive behaviour is exhibited for $0 < H < 1/2$, superdiffusive behaviour for $1/2 < H \leq 1$, and normal Brownian motion is obtained when $H = 1/2$. The Hurst exponent, H, is related to the latent dimension (Mandelbrot 1984) of the random walk, d_w, through (Voss 1989)

$$H = \frac{1}{d_w}. \tag{2}$$

The walk dimension, also called by other authors the trail or path dimension, is the fractal dimension of the curve described by a random walker in space, parametrised by time.

Such dynamical behaviour may be caused by normal Brownian motion confined to a fractal space of dimension d_f, and it is this type of system, where $d_w \geq 2$, in which our interest here lies. It is our desire in this paper to make some predictions in the context of pulsed-field-gradient (PFG) NMR for the q-space behaviour (Callaghan *et al.* 1992) of diffusion in fractal spaces. The motivation for this stems from the recognition

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that several structures which are frequently investigated using NMR techniques, such as porous media, lung tissue and smectic liquid crystals, have been found to possess fractal characteristics.

The fractional diffusion equation and solutions

Our results are based on the work of Metzler *et al.* (1994), who obtained and solved the fractional diffusion equation

$$\frac{\partial^{2/d_w}}{\partial t^{2/d_w}} P(r,t) = \frac{\kappa}{r^{d_s-1}} \frac{\partial}{\partial r} \left(r^{d_s-1} \frac{\partial}{\partial r} P(r,t) \right), \tag{3}$$

where κ is a fractional diffusion coefficient (dependent on d_w), where d_s is the spectral or fracton dimension (Alexander & Orbach 1982; Ben-Avraham & Havlin 1983; Rammal & Toulouse 1983), and is given by

$$d_s = \frac{2d_f}{d_w}. \tag{4}$$

The derivation of (3) was achieved largely heuristically, guided by some empirical results of computer simulations and scaling arguments. The solution was given in the form of an H-function as (see appendix and Mathai & Saxena 1978)

$$P(r,t) = \frac{d_w (2\kappa^{1/2} t^{1/d_w})^{-d_f}}{\Gamma(1 - d_f/d_w + d_f/2)\Gamma(d_f/2)} H^{2,0}_{1,2} \left[\frac{r^{d_w}}{2^{d_w} \kappa^{d_w/2} t} \middle| \begin{array}{l} (1 - \frac{d_f}{d_w}, 1) \\ (1 - \frac{d_f}{d_w}, \frac{d_w}{2}), (0, \frac{d_w}{2}) \end{array} \right], \tag{5}$$

where $P(r,t) r^{d_f - 1} \mathrm{d}r$ is the probability of a particle having a displacement between r and $r + \mathrm{d}r$ at time t. It is implicitly assumed that the displacement is zero at $t = 0$. (Here, our $P(r,t)$ differs from Metzler *et al.*'s, except for the inclusion of κ, because of errors on their part in obtaining the normalisation factor, and in omitting the numerical factor in the argument of the H-function.)

In the context of PFG NMR, in general, it would not be $P(r,t)$ which is measured but a one-dimensional projection of this along, say, the z-axis. This projection may be obtained either by directly integrating $P(r,t)$ or by subtracting 2 from the *spectral dimension* in the diffusion equation (3) and solving. In either case, the result is (assuming $2 < d_f \leq 3$)

$$\Phi(\zeta, t) = a(t) H^{2,0}_{1,2} \left[\frac{\zeta^{d_w}}{2^{d_w} \kappa^{d_w/2} t} \middle| \begin{array}{l} (1 - \frac{d_f}{d_w} + \frac{2}{d_w}, 1) \\ (2 - \frac{d_f}{d_w}, \frac{d_w}{2}), (0, \frac{d_w}{2}) \end{array} \right], \tag{6}$$

$$a(t) = \frac{d_w (2\kappa^{1/2} t^{1/d_w})^{2-d_f}}{\Gamma(1 - d_f/d_w + d_f/2)\Gamma(d_f/2 - 1)}, \tag{7}$$

where $\Phi(\zeta, t)\zeta^{d_f - 3} \mathrm{d}\zeta$ is the probability of a particle having a displacement in the z-direction between ζ and $\zeta + \mathrm{d}\zeta$ at time t. We would prefer to re-define $\Phi(\zeta, t)$ such that

$$\psi(\zeta, t) = \zeta^{d_f - 3} \Phi(\zeta, t), \tag{8}$$

so that the normalisation condition is simply

$$\int_0^\infty \psi(\zeta,t)\mathrm{d}\zeta = 1. \tag{9}$$

For this density function we obtain for the mean-square-displacement

$$< \zeta^2(t) >= \frac{4(d_f/2-1)(1+d_f/2-d_f/d_w)}{\Gamma(1+2/d_w)}\kappa t^{2/d_w}, \tag{10}$$

where it should be noted that κ is not equivalent to the normal diffusion coefficient unless $d_w = 2$.

Using the series expansion (38) for H-functions given in the appendix, we may re-write $\psi(\zeta,t)$ in the form

$$\begin{aligned}\psi(\zeta,t) &= a(t)\zeta^{d_f-3} \\ &\sum_{\nu=0}^{\infty}\frac{\Gamma(d_f/d_w-2-\nu)}{\Gamma(1-d_f/d_w-2/d_w(1-d_f/d_w+\nu))}\frac{(-1)^\nu}{\nu!}\left(\frac{\zeta}{2\kappa^{1/2}t^{1/d_w}}\right)^{2(2-d_f/d_w+\nu)} \\ &+\frac{\Gamma(2-d_f/d_w-\nu)}{\Gamma(1-d_f/d_w-2/d_w(\nu-1))}\frac{(-1)^\nu}{\nu!}\left(\frac{\zeta}{2\kappa^{1/2}t^{1/d_w}}\right)^{2\nu}.\end{aligned} \tag{11}$$

It now becomes apparent that in the limit of $\zeta \ll 2\kappa^{1/2}t^{1/d_w}$, $\psi(\zeta,t)$ obeys a power law:

$$\psi(\zeta,t) \sim a(t)\zeta^{d_f-3}. \tag{12}$$

From this, it can be seen that for $d_f < 3$ the density has a "weak" singularity at $\zeta = 0$, where by "weak" we mean that the density is normalisable.

q-space behaviour

Previous attempts (Banavar *et al.* 1985; Jug 1986; Kärger & Vojta 1987; Kärger *et al.* 1988; Widom & Chen 1995) to address the issue of the form of the NMR signal decay, $S(q,\Delta)$, due to fractional Brownian motion, as measured in a PFG experiment, have all concluded similarly that

$$S(q,\Delta) \sim \exp(-cq^2\Delta^{2/d_w}), \tag{13}$$

where $q = \gamma g\delta/2\pi$, γ is the gyromagnetic ratio, g is the magnetic-field-gradient strength, δ is the time duration of the gradient pulses, Δ is the gradient pulse separation time, and c is a constant. It will become clear, however, that we present here a somewhat different conclusion.

In the narrow-pulse approximation, $\delta \ll \Delta$, $S(q,\Delta)$, has a Fourier transform relation with the probability density for displacements, and is given by

$$S(q,\Delta) = \int \psi(\zeta,\Delta)\mathrm{e}^{i2\pi q\zeta}\mathrm{d}\zeta. \tag{14}$$

Thus, we may directly obtain $S(q,\Delta)$ by Fourier transforming $\psi(\zeta,\Delta)$. Using the Fourier relationships for H-functions as given by Glöcke & Nonnenmacher (1993), one obtains

$$S(q,\Delta) = \pi\sigma H^{1,2}_{3,3}\left[4\pi q\kappa^{1/2}\Delta^{1/d_w}\left|\begin{array}{l}(\frac{d_f}{d_w}-\frac{d_f}{2},\frac{1}{2}),(2-\frac{d_f}{2},\frac{1}{2}),(\frac{1}{2},\frac{1}{2})\\(0,1),(0,\frac{1}{d_w}),(\frac{1}{2},\frac{1}{2})\end{array}\right.\right], \tag{15}$$

$$\sigma = \frac{1}{\Gamma(1-d_f/d_w+d_f/2)\Gamma(d_f/2-1)}. \tag{16}$$

Again, employing the series expansion (38), it can be shown that (15) may be expressed as

$$S(q,\Delta) = \pi^{1/2}\sigma\sum_{\nu=0}^{\infty}\frac{\Gamma(1-d_f/d_w+d_f/2+\nu)\Gamma(d_f/2-1+\nu)}{\Gamma(1+2\nu/d_w)\Gamma(1/2+\nu)}\frac{(-1)^\nu}{\nu!}(2\pi q\kappa^{1/2}\Delta^{1/d_w})^{2\nu}, \tag{17}$$

from which it is readily found that for $d_f = 3$ and $d_w = 2$ the usual result is obtained:

$$S(q,\Delta) = \exp(-4\pi q^2 D\Delta), \tag{18}$$

where, since $d_w = 2$, we have equated κ with the familiar diffusion coefficient D.

An interesting feature of the behaviour of $S(q,\Delta)$ is now observed for large $q\Delta^{1/d_w}$. From Mathai & Saxena (1978), we have for large x and $n \neq 0$

$$H^{m,n}_{p,q}\left[x\left|\begin{array}{c}(a_p,A_p)\\(b_q,B_q)\end{array}\right.\right] \sim |x|^\alpha, \tag{19}$$

where

$$\alpha = \max\left(\frac{a_j-1}{A_j}\right)\ ;\ j=1,...,n. \tag{20}$$

We easily find that in this asymptotic limit, $4\pi q\kappa^{1/2}\Delta^{1/d_w} \gg 1$,

$$S(q,\Delta) \sim (q\kappa^{1/2}\Delta^{1/d_w})^{2-d_f}\quad;\quad 2 < d_f < 3. \tag{21}$$

This is, of course, just the reciprocal-space complement of the small ζ limit given in (12). It is interesting to note that this power law behaviour is similar to that predicted for scattering from volume-fractal structures (Sinha 1989) and, in particular, is absent from previous theories (*cf.* equation (13)).

The scattering analogy

Analogies with PFG NMR and scattering or diffraction have previously been observed (Callaghan *et al.* 1992), and it is possible to provide an alternative derivation of the power law in (21) using these ideas.

For the PFG experiment,

$$S(q,\Delta) = \int\int\phi(z_0)W(z|z_0,\Delta)\mathrm{e}^{i2\pi q(z-z_0)}\mathrm{d}z\mathrm{d}z_0, \tag{22}$$

where $\phi(z_0)\mathrm{d}z_0$ is the probability of finding a particle initially between positions z_0 and $z_0 + \mathrm{d}z_0$, and $W(z|z_0, \Delta)\mathrm{d}z$ is the conditional probability of locating a particle between z and $z + \mathrm{d}z$ given that at a time Δ earlier it was at z_0. We may re-express this in terms of the displacement ζ as

$$S(q, \Delta) = \int \int \phi(z_0) W(z_0 + \zeta | z_0, \Delta) \mathrm{e}^{i2\pi q\zeta} \mathrm{d}\zeta \mathrm{d}z_0. \tag{23}$$

In the limit that ζ is much less than the root-mean-square displacement, W becomes dependent upon the final position only, that is,

$$W(z_0 + \zeta | z_0, \Delta) \sim \phi(z_0 + \zeta). \tag{24}$$

We may now re-write (23) inserting the one-dimensional space autocorrelation function,

$$c(\zeta) \sim \int \phi(z_0)\phi(z_0 + \zeta)\mathrm{d}z_0, \tag{25}$$

as

$$S(q, \Delta) \sim \int c(\zeta) \mathrm{e}^{i2\pi q\zeta} \mathrm{d}\zeta. \tag{26}$$

In scattering terminology, this would be a one-dimensional equivalent of the structure factor, and it is this which gives rise to the diffraction-like peaks observed in some PFG experiments.

For a space which behaves as a volume fractal the autocorrelation function is expected to decay according to the power law (Takayasu 1989)

$$c(\zeta) \sim \zeta^{d_f - 3}, \tag{27}$$

which, one might note, is consistent with (12), and thus as expected, upon substituting this into (26) we find

$$S(q, \Delta) \sim q^{2 - d_f}. \tag{28}$$

Also, the condition placed on ζ, that it must be much less than the root-mean-square displacement, implies the corresponding condition for q,

$$q \gg \frac{1}{< \zeta^2 >^{1/2}}. \tag{29}$$

Thus, we have verified somewhat the predictions based on the work of Metzler *et al.*, and have also gained a little insight into the existence of the large q limit.

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Appendix: the H-function

We provide here a definition of the H-function. (For further details see Mathai & Saxena 1978.) The H-function is a very general function and contains as special cases many of the special functions. It is related to an inverse Mellin transform as follows:

$$\begin{aligned} H^{m,n}_{p,q}[z] &= H^{m,n}_{p,q}\left[z \,\middle|\, \begin{matrix} (a_p, A_p) \\ (b_q, B_q) \end{matrix} \right] \\ &= H^{m,n}_{p,q}\left[z \,\middle|\, \begin{matrix} (a_1, A_1), (a_2, A_2), ..., (a_p, A_p) \\ (b_1, B_1), (b_2, B_2), ..., (b_q, B_q) \end{matrix} \right] \\ &= \frac{1}{2\pi i} \oint_C \chi(s) z^s \mathrm{d}s, \end{aligned} \tag{30}$$

where

$$\chi(s) = \frac{\prod_{j=1}^{m} \Gamma(b_j - B_j s) \prod_{j=1}^{n} \Gamma(1 - a_j + A_j s)}{\prod_{j=m+1}^{q} \Gamma(1 - b_j + B_j s) \prod_{j=n+1}^{p} \Gamma(a_j - A_j s)}, \tag{31}$$

where an empty product is taken as unity. In the above, the indices m, n, p, q are positive integers such that $0 \le n \le p$, $1 \le m \le q$, the parameters A_j $(j = 1, ..., p)$, B_j $(j = 1, ..., q)$ are positive real numbers, and a_j $(j = 1, ..., p)$, b_j $(j = 1, ..., q)$ are complex numbers such that

$$\begin{gathered} A_j(b_h + \nu) \neq B_h(a_j - \lambda - 1), \\ \nu, \lambda = 0, 1, 2... \; ; \; h = 1, ..., m \; ; \; j = 1, ..., n. \end{gathered} \tag{32}$$

C is a contour separating the points for which $\chi(s)$ is singular,

$$s = \frac{b_j + \nu}{B_j} \; ; \quad j = 1, ..., m \; ; \; \nu = 0, 1, ... \; , \tag{33}$$

and

$$s = \frac{a_j - \nu - 1}{A_j} \; ; \quad j = 1, ..., n \; ; \; \nu = 0, 1, ... \; . \tag{34}$$

The H-function is analytic for $z \neq 0$ if $\mu > 0$, or for $0 < |z| < \beta^{-1}$ if $\mu = 0$, where

$$\mu = \sum_{j=1}^{q} B_j - \sum_{j=1}^{p} A_j \tag{35}$$

and

$$\beta = \prod_{j=1}^{p} A_j^{A_j} \prod_{j=1}^{q} B_j^{-B_j}. \tag{36}$$

The H-function may be expressed in series form (Braaksma 1964) provided that

$$\begin{gathered} B_j(b_h + \nu) \neq B_h(b_j + \lambda) \\ \nu, \lambda = 0, 1, 2... \; ; \; j \neq h \; ; \; j, h = 1, ..., m. \end{gathered} \tag{37}$$

This being satisfied, we then have

$$
\begin{aligned}
H_{p,q}^{m,n}[z] \quad &= \\
&\sum_{h=1}^{m}\sum_{\nu=0}^{\infty} \frac{\prod_{j(\neq h)=1}^{m} \Gamma(b_j - B_j(b_h+\nu)/B_h) \prod_{j=1}^{n} \Gamma(1-a_j+A_j(b_h+\nu)/B_h)}{\prod_{j=m+1}^{q} \Gamma(1-b_j+B_j(b_h+\nu)/B_h) \prod_{j=n+1}^{p} \Gamma(a_j - A_j(b_h+\nu)/B_h)} \\
&\times \frac{(-1)^{\nu} z^{(b_h+\nu)/B_h}}{\nu! B_h}. \qquad (38)
\end{aligned}
$$

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