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Anomalous Scaling in Systems Partially Controlled by Diffusion

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We study the nature of anomalous scaling in several systems partially controlled by diffusion. We quantify the departure from Fickian scaling by means of an apparent exponent governing the scaling of long-time behavior with system size. We find that anomalous scaling should be expected whenever complex geometries, higher dimensionality, or time-dependent boundary conditions are encountered.

KEY WORDS: Diffusion; scaling.

1. INTRODUCTION

An elementary result in the theory of diffusive systems is that the asymptotic time dependence of functionals of the concentration scales as the square of some length characteristic of the system size. However, it has long been known[(1)] that anomalous scaling arises in permeation or sorption problems with, for example, time-dependent boundary conditions. Similar behavior is also seen in reaction-diffusion systems and in spatially inhomogeneous systems.

In an effort to characterize this departure from the naive scaling form, we consider several elementary problems in diffusive systems, including both time-independent and radiation boundary conditions and a simple reaction-diffusion system. We quantify the observed behavior through various logarithmic derivatives, which in turn produce certain slowly varying functions which, at least locally in the system size, play the role of apparent scaling exponents.

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Furthermore, these apparent local scaling exponents can in some cases be interpreted as governing the scaling of some part of the mass of the random walk problem isomorphic to the diffusive system under consideration, so that this behavior is reminiscent of the scaling seen in truly fractal systems. These apparent exponents are of course not scale invariant, and there is no *a priori* fractal character to any of the simple systems we study. However, experimental data corresponding to such systems might easily be interpreted in the light of fractal scaling, suggesting to the experimentalist the application of concepts from fractal geometry as predictive tools. Moreover, our elementary but occasionally counterintuitive results suggest the origin of nonclassical scaling exponents in systems where there is no underlying fractal structure.

In one dimension, our model system is a planar slab of material initially devoid of diffusing solute, i.e., $c(x, t=0)=0$, $0<x<l$, with various boundary conditions imposed at $x=0$ and $x=l$. The primary quantities of interest are the flux per unit area at $x=l$,

$$J(l, t)= -D(\partial c/\partial t)_l \tag{1.1}$$

and the total mass transport across that boundary,

$$Q(t)=\int_0^t J(l, t')\, dt' \tag{1.2}$$

In $d>2$, our model is a cylindrical shell, a spherical shell, or a higher dimensional analog. In general, we consider transport equations of the form

$$\partial c/\partial t=\mathscr{L}_x c(x, t) \tag{1.3}$$

where $\mathscr{L}_x$ is an operator of mixed differential and algebraic type, linear in x. Problems of this type are often readily solved in Laplace transform, resulting, for example, in an expression for the Laplace transform of $J(x, t)$:

$$\hat{J}(x; p)=\frac{1}{p}\frac{f(x; p)}{\Delta(p)}=\int_0^\infty e^{-pt} J(x, t)\, dt \tag{1.4}$$

$J(x, t)$ is obtained by evaluating the corresponding Bromwitch integral, with the result that

$$J(x, t)=\frac{f(x; 0)}{\Delta(0)}+\sum_{n=1}^{\infty}\frac{1}{p_n}\frac{f(x; p_n)}{(\partial\Delta/\partial p)_{p_n}}\exp(p_n t) \tag{1.5}$$

where the p_n are the ordered distinct roots of $\Delta(p)=0$ and $f(x; 0)/\Delta(0)$ is the asymptotic steady-state solution J_s.

For the problems we consider, the roots p_n are all negative. Thus, at long times, the approach to equilibrium is dominated by the root nearest the origin, p_1, or

$$J(x, t) - J_s \xrightarrow[t \to \infty]{} C_1(x) e^{-|p_1| t} \tag{1.6}$$

Thus, a semilogarithmic plot of $|J(x, t) - J_s|$ against time is expected to be asymptotically linear with slope $-|p_1|$. Ultimately, it is the dependence of $|p_1|$ on l that we seek. However, $\Delta(p) = 0$ is, in general, a transcendental equation, and simple expressions for p_1 are not to be had.

An alternative exists in the time lag,[2] which characterizes the approach of a system to equilibrium and is given by

$$L(x) = \frac{1}{J_s} \int_0^\infty [J_s - J(x, t)]\, dt \tag{1.7}$$

The time lag has the advantage that it can often be obtained exactly, frequently in algebraic form. We are primarily interested in $L(l)$, although another characteristic time is the mean first passage time,[2]

$$\bar{t}(l) = L(l) - L(0) \tag{1.8}$$

In the next section, we report on scaling results for permeation problems with time-independent boundary conditions, and in Section 3 we present our results for problems with radiation boundary conditions. Section 4 is devoted to a simple reaction-diffusion problem.

2. TIME-INDEPENDENT BOUNDARY CONDITIONS

Consider diffusion through a slab of thickness l, with the concentration obeying

$$D \frac{\partial^2 c}{\partial x^2} = \frac{\partial c}{\partial t} \tag{2.1}$$

and subject to the initial and boundary conditions

$$\begin{aligned} c(x, 0) &= 0 \\ c(0, t) &= c_0 \\ c(l, t) &= 0 \end{aligned} \tag{2.2}$$

Then the Laplace transform of the flux is found to be

$$\hat{J}(x) = \frac{Dc_0}{p} \frac{q \cosh q(l-x)}{\sinh ql} \tag{2.3}$$

where $q = (p/D)^{1/2}$. The roots of $\Delta(p) = \sinh ql$ are readily found to be

$$q_n = in\pi/l \tag{2.4}$$

or

$$p_n = -n^2\pi^2 D/l^2 \tag{2.5}$$

so that

$$J(x, t) = \frac{Dc_0}{l} - 2\frac{Dc_0}{l} \sum_{n=1}^{\infty} \cos\frac{n\pi x}{l} e^{-n^2\pi^2 Dt/l^2} \tag{2.6}$$

Thus, $J(x, t) - J_s$ scales asymptotically as $C_1(x) \exp(-\pi^2 Dt/l^2)$, $\ln|J(x, t) - J_s|$ is asymptotically linear with slope $-|p_1| = -\pi^2 Dt/l^2$, and $|p_1|$ scales as l^{-2}, or the asymptotic time dependence of $J(x, t)$ scales as l^2. Similarly, the time lag at l is found to be

$$L(l) = l^2/6D \tag{2.7}$$

and the mean time of first passage is the familiar Einstein result

$$\bar{t}(l) = l^2/2D \tag{2.8}$$

These standard results mirror the scaling of an unbiased random walk, in which the mean square displacement of the walker is linear in time,

$$\langle R^2 \rangle \sim t \tag{2.9}$$

so that the time for a random walker to traverse a system of length l should scale as $t_l \sim l^2$. Finally, since the "mass" of the trajectory of the random walker is linear in t, we have $M(l) \sim l^2 \equiv l^{d_f}$, where $M(l)$ is the mass of a trajectory of linear scale l, and d_f is the fractal dimension of the random walk. For unbiased random walks in any Euclidean dimension, $d_f = \partial \ln M(l)/\partial \ln l \equiv 2$.

Estimators of d_f, exact for this simple model, are provided by

$$\begin{aligned} \nu_p &= -\partial \ln p_1/\partial \ln l \\ \nu_L &= \partial \ln L(l)/\partial \ln l \\ \nu_{\bar{t}} &= \partial \ln \bar{t}(l)/\partial \ln l \end{aligned} \tag{2.10}$$

It is interesting to ask the effects of dimensionality and geometry on these results. We extend our simple slab-geometry results to a cylindrical shell, a spherical shell, and higher dimensional analogs. In d dimensions, Eq. (2.1) is replaced by

$$\frac{\partial c}{\partial t} = r^{-\beta} \frac{\partial}{\partial r}\left(r^{\beta} D \frac{\partial c}{\partial r}\right) \tag{2.11}$$

where $\beta = d-1$. The boundary and initial conditions analogous to those given in Eq. (2.2) are now

$$\begin{aligned} c(r, 0) &= 0, \qquad a < r < b \\ c(a, t) &= c_a \\ c(b, t) &= 0 \end{aligned} \tag{2.12}$$

Applying the method of Frisch,[2] we find the time lag to be

$$L(b, a) = \frac{1}{D I_d} \int_a^b r^{-\beta} \int_r^b x^{\beta} \int_x^b y^{-\beta}\, dy\, dx\, dr \tag{2.13}$$

where

$$I_d = \int_a^b r^{-\beta}\, dr \tag{2.14}$$

We note in passing that $\lim_{d \to \infty} L(b, a) = (b^2 - a^2)/2d\, D$.

In $d = 3$, the time lag is $L(b, a) = (b-a)^2/6D$, a result identical in form to the one-dimensional result (2.7). However, in no other dimension $d > 1$ is the time lag a function of $b - a$. Thus, only in $d = 1$ and $d = 3$ is there a single length with which to characterize the system. We take as an appropriate generalization of the second equation in (2.10) for the apparent scaling exponent $\nu_L = \partial \ln L / \partial \ln V$, where $V = \Gamma_d(b^d - a^d)$, so that

$$\nu_L = \frac{b^d - a^d}{L\, d b^{d-1}} \frac{\partial L}{\partial b} \tag{2.15}$$

with a held fixed. Only in $d = 1$ is ν_L a constant. In the limit $b/a \to 1$, the volume is linear in the shell thickness, and $\nu_L \to 2$, independent of dimension. In the limit $b/a \to \infty$, the volume becomes proportional to b^d, and $\nu_L \to 2/d$. It is interesting to note, however, that if the concentration at $r = b$ is nonzero, then in this limit $\nu_L \to 2$ also. Plotted in Fig. 1 as a function of b/a is ν_L for $d = 2$, 3, and 4.

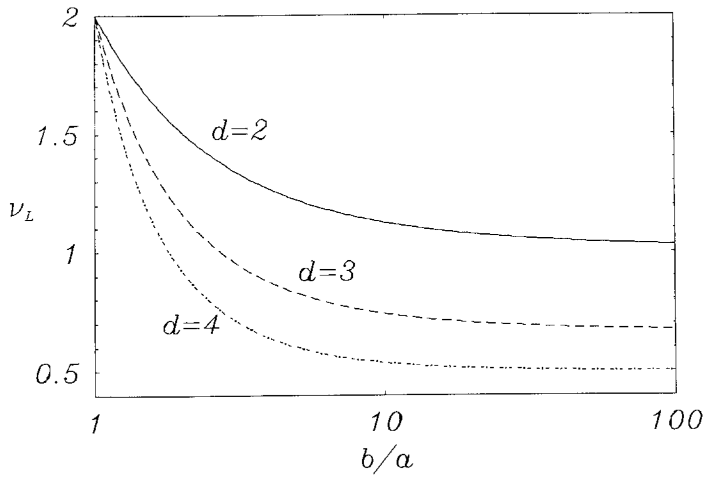

Fig. 1. Apparent scaling exponent ν_L for shell geometries in dimensions $d = 2$, 3, and 4 as a function of b/a. The concentration is fixed at $r = a$ and is taken to be 0 at $r = b$.

Thus we see that complex non-Fickian scaling can be introduced even by simple geometric considerations. In subsequent sections, we will see how the introduction of nondiffusive elements, such as time-dependent boundary conditions and chemical reactions, can also affect observed scaling behavior.

3. RADIATION BOUNDARY CONDITIONS

Now let us investigate the effect of time-dependent boundary conditions on the asymptotic time dependence of the flux. Consider a system obeying the diffusion equation (2.1) as before, but now with the initial and boundary conditions

$$\begin{aligned} c(x, 0) &= 0 \\ \left(\frac{\partial c}{\partial x}\right)_0 &= h(c(0, t) - c_0) \\ c(l, t) &= 0 \end{aligned} \tag{3.1}$$

The Laplace transform of the flux is now found to be

$$\hat{J}(x) = \frac{Dc_0}{p} \frac{hq \cosh q(l-x)}{h \sinh ql + q \cosh ql} \tag{3.2}$$

where, as before, $q=(p/D)^{1/2}$. The roots of $\Delta(p)=h\sinh ql+q\cosh ql$ are now, in general, only to be found numerically, so we consider the time lag, which is found to be

$$L(l)=\frac{l^2}{6D}\frac{s+3}{s+1} \tag{3.3}$$

where $s=hl$. Then $\nu_L=\partial\ln L(l)/\partial\ln l$ is found to be

$$\nu_L=2\frac{s^2+3s+3}{s^2+4s+3} \tag{3.4}$$

In the limits $s\to 0$ and $s\to\infty$ we recover the naive form $\nu_L\to 2$. The former limit is a null problem, and the latter limit is the system discussed in the preceding section. However, ν_L attains a minimum of $\nu_L=\sqrt{3}$ at $s=\sqrt{3}$, as seen in Fig. 2. Also shown in Fig. 2 is

$$\begin{aligned}\nu_p&=-\partial\ln p_1/\partial\ln l\\&=2(s^2-q_1^2l^2)/(s^2-q_1^2l^2+s)\end{aligned} \tag{3.5}$$

which is seen from the form of $\Delta(p)$ to depend only on $s=hl$. As can be seen, ν_L and ν_p have qualitatively similar behavior. Finally, we note that $\bar{t}(l)=l^2/2D$ for this system, an unsurprising result, as walkers contributing to an estimator of first passage times will not interact strongly with the boundary conditions at $x=0$.

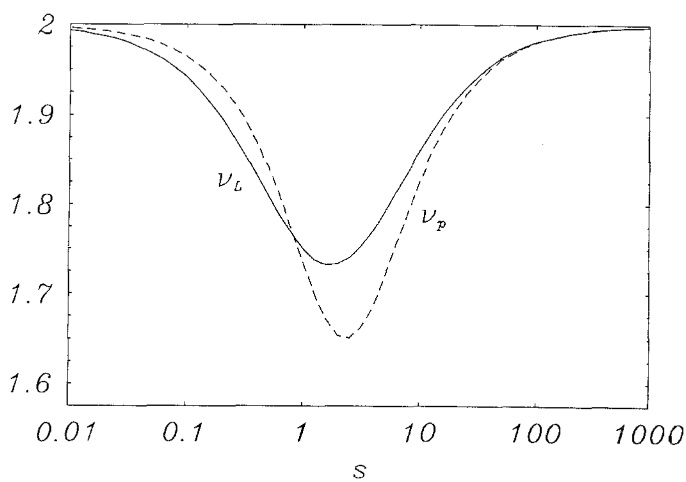

Fig. 2. Apparent scaling exponents ν_L and ν_p for a one-dimensional model with radiation boundary conditions at $x=0$ as functions of $s=hl$.

Extending our results to the shall geometries discussed in the previous section, we find that the boundary and initial conditions analogous to those given in Eq. (3.1) become

$$\begin{aligned} &c(r, 0) = 0, \qquad a < r < b \\ &\left(r^{\beta} \frac{\partial c}{\partial r}\right)_a = h(c(a, t) - c_a) \\ &c(b, t) = 0 \end{aligned} \tag{3.6}$$

Applying the method of Frisch,[2] we find the time lag to be

$$\begin{aligned} L(b, a) = \frac{1}{D(1 + hI_d)} \bigg(&\int_a^b x^{\beta} \int_x^b y^{-\beta}\, dy\, dx \\ &+ h \int_a^b r^{-\beta} \int_r^b x^{\beta} \int_x^b y^{-\beta}\, dy\, dx\, dr \bigg) \end{aligned} \tag{3.7}$$

where I_d is given by Eq. (2.14). The apparent scaling exponent ν_L is again given by Eq. (2.15). In dimensions $d > 1$, there is no natural scaling variable independent of h, although, as in the case of time-independent boundary conditions, $\nu_L \to 2$ as $b/a \to 1$, and $\nu_L \to 2/d$ as $b/a \to \infty$. Plotted in Fig. 3 as functions of b/a are $\nu_L(h = 0)$, $\nu_L(h = 1)$, and $\nu_L(h \to \infty)$ for $d = 2$. (Note that $h \to \infty$ is the case studied in the preceding section.) We see that the scaling does not depend strongly on h, with the strongest

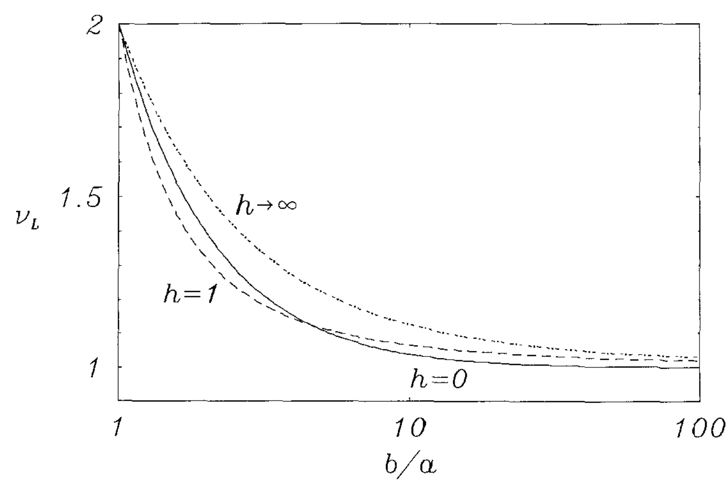

Fig. 3. Apparent scaling exponent ν_L in $d = 2$ for various values of h as a function of b/a. Radiation boundary conditions hold at $r = a$, while $c(b, t) = 0$.

dependence being for small b/a. These results are qualitatively similar to those for higher dimensions, where the dependence on h becomes even less pronounced and, as indicated above, ν_L tends asymptotically to $2/d$.

As a further example of the effect of radiation boundary conditions, let us return to the one-dimensional case and modify the boundary condition at $x=l$ to be

$$\left(\frac{\partial c}{\partial x}\right)_l = -h(c(l, t) - c_l) \tag{3.8}$$

the initial conditions and boundary condition at $x=0$ being given as in Eq. (3.1). We find the time lag at l to be

$$L(l) = \frac{l^2}{6D} \frac{6(c_0 + c_l)(1+s) + (c_0 + 2c_l)s^2}{(c_0 - c_l)\, s(2+s)} \tag{3.9}$$

where $s = hl$. We find ν_L to be

$$\nu_L = \frac{2}{2+s} \frac{(c_0 + c_l)(s^3 + 6s^2 + 12s + 6) + c_l s^2(s+3)}{(c_0 + c_l)(s^2 + 6s + 6) + c_l s^2} \tag{3.10}$$

which tends, as before, to 2 as $s = hl \to \infty$. However, in the opposite limit of $s \to 0$, $\nu_L = 1$.

Similar behavior is found in the mean first passage time,

$$\bar{t}(l) = \frac{l^2}{2D} \frac{c_0 + c_l}{c_0 - c_l} \frac{2+s}{s} \tag{3.11}$$

for which

$$\nu_{\bar{t}} = 2\,\frac{1+s}{2+s} \tag{3.12}$$

which has the same limiting values as ν_L.

Extending these results to dimensions $d > 1$ is also possible; the modification to the boundary condition (3.6) analogous to (3.8) is

$$\left(r^\beta \frac{\partial c}{\partial r}\right)_b = -h(c(b, t) - c_b) \tag{3.13}$$

We present graphical results only for the case $c_b = 0$ and $h = 1$ in Fig. 4 for dimensions $d = 2, 3$, and 4. As noted above, in $d = 1$, $\nu_L \to 2$ as $l \to \infty$. However, in $d > 1$, $\nu_L \to 1$ as $b/a \to \infty$. The value of b/a for which ν_L is a maximum approaches unity as $d \to \infty$, and the magnitude of the effect is seen to diminish in higher dimensions.

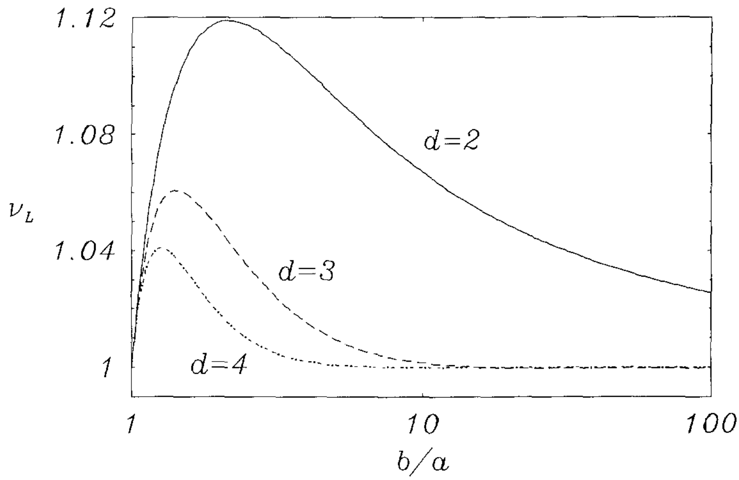

Fig. 4. Apparent scaling exponent ν_L for shell geometries in dimensions $d=2$, 3, and 4 as a function of b/a. Radiation boundary conditions hold on both inner and outer surfaces. In each case shown here, $h=1$ and $c_b=0$.

What is the significance of these results? If one makes measurements of the time lag (for a one-dimensional system) in an infinitesimal neighborhood of some l_0, the values obtained will appear to scale as $l^{\nu_L(l=l_0)}$. Similarly, the asymptotic time dependence of the flux will appear to scale as $l^{\nu_p(l=l_0)}$. Thus, ν_L and ν_p are seen to behave as fractal dimensions, albeit only locally in l. However, a class of systems of experimental interest may not span several orders of magnitude in l or hl, but may be restricted to a range of no more than an order of magnitude where ν_L and ν_p may be slowly varying. Thus, systems that are not truly fractal may appear so, and well-developed concepts from fractal geometry and scaling may be employed as predictive tools in describing the behavior of an entire class of experimental systems.

The degree to which the time dependence of a one-dimensional system does not scale as l^2 can also be taken as a measure of the importance of the boundary conditions, and suggests ranges over which one may ignore the full radiation boundary conditions and approximate a system by a less general model.

In dimensions $d>1$, the added term in the Laplacian $[(d-1)/r]\ \partial/\partial r$ is responsible for the unusual scaling observed for both time-independent and radiation boundary conditions. Thus, one should expect complex scaling whenever higher dimensions and complicated geometries are encountered, irrespective of the nature of the boundary conditions, which are also seen to affect the scaling.

Since every diffusion problem is isomorphic to some random walk problem and the fractal dimension of an unbiased random walk in Euclidean space is known to be 2, it is tempting to ask where the missing dimensionality appears. We have already investigated the case of a slab composed of two distinct lamina for the particular problem of desorption from the first region through the second.[3] There, the time-dependent boundary conditions arise at the internal interface. Separate exponents are found for the left- and right-hand regions, and their sum is 2, so that the deviation of the individual exponents from 2 represents a partitioning of the mass of the equivalent random walk between the two regions.

In the one-dimensional problems with radiation boundary conditions which we have investigated here, the missing dimensionality must appear in the half-spaces connected to the slab by radiation boundary conditions. The limits $hl \to 0$ and $hl \to \infty$ effectively decouple the slab from those half-spaces. However, the ideal treatment of the boundary conditions precludes concentration fluctuations in those half-spaces, and so the missing dimensionality is lost to our analysis.

4. REACTION DIFFUSION

Another case where anomalous scaling can be expected is in a system in which a chemical reaction is driven by a diffusive process. As a simplest case, consider an irreversible first-order reaction, for which the concentration obeys the partial differential equation

$$D\frac{\partial^2 c}{\partial x^2} - kc(x, t) = \frac{\partial c}{\partial t} \tag{4.1}$$

We consider the permeation problem with initial and boundary conditions given by (2.2).

The Laplace transform of the flux is found to be identical to (2.3), only now $q = [(p+k)/D]^{1/2}$. Thus,

$$p_n = -k - n^2\pi^2 D/l^2 \tag{4.2}$$

so that, apart from the constant shift by k, the scaling of the p_n is as one would expect. However, the time lag at l is found to be

$$L(l) = \frac{l^2}{2D}\frac{u \cosh u - \sinh u}{u^2 \sinh u} \tag{4.3}$$

and the mean first passage time is

$$\bar{t}(l) = \frac{l^2}{2D}\frac{\sinh u}{u \cosh u} \tag{4.4}$$

where $u=(kl^2/D)^{1/2}$. The corresponding apparent exponents are

$$\nu_L=\frac{u}{\sinh u}\frac{\cosh u\sinh u-u}{u\cosh u-\sinh u} \tag{4.5}$$

and

$$\nu_{\bar{t}}= =\frac{\cosh u\sinh u+u}{\cosh u\sinh u} \tag{4.6}$$

Both of these apparent exponents tend to 2 in the limit $u\to 0$, while in the limit $u\to\infty$, they tend to 1. These results are illustrated in Fig. 5.

If we denote by $v(x,t)$ the bound or reacted species, then v satisfies the simple differential equation $kc=\partial v/\partial t$. Then the total reacted mass $V(t)=\int_0^l v(x,t)\,dx$ has a time lag

$$L_V=\frac{l^2}{2D}\frac{\sinh u-u}{u^2\sinh u} \tag{4.7}$$

so that its corresponding apparent exponent is

$$\nu_V=\frac{u}{\sinh u}\frac{u\cosh u-\sinh u}{\sinh u-u} \tag{4.8}$$

ν_V also tends to 2 in the limit $u\to 0$. However, $\nu_V\to 0$ as $u\to\infty$. As our result for ν_V suggests, we have thus been unable to ascribe any significance

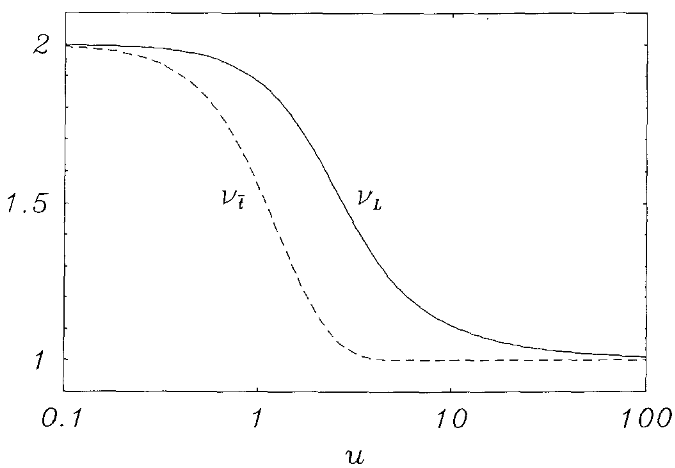

Fig. 5. Apparent scaling exponents $\nu_{\bar{t}}$ and ν_L for a one-dimensional reaction-diffusion system as functions of $u=(kl^2/D)^{1/2}$.

to v_L (or $v_{\bar{l}}$) and v_V as a partitioning of the mass of the random walk between a free part and a bound part.

Nevertheless, our results have obvious practical implications. One can imagine, for example, a protective coating which scavenges some undesirable diffusant by means of a first-order reaction. If the species is of sufficiently high reactivity and low mobility, then the exit flux will be inversely proportional to the coating thickness, but the total reacted mass will be independent of the coating thickness.

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REFERENCES

1. H. L. Frisch, *J. Chem. Phys.* **37**:2408 (1962).
2. H. L. Frisch, *J. Chem. Phys.* **36**:510 (1962).
3. G. O. Williams, H. L. Frisch, and H. Ogawa, *J. Colloid Interface Sci.* **123**:448 (1988).