Separation Science and Technology
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713708471

Transport Equations in Chromatography with a Finite Speed of Signal Propagation

Jaume Masoliver[a]; George H. Weiss[b]
[a] DEPARTMENT DE FISICA FONAMENTAL, UNIVERSITAT DE BARCELONA DIAGONAL, BARCELONA, SPAIN [b] NATIONAL INSTITUTES OF HEALTH BETHESDA, MARYLAND

To cite this Article Masoliver, Jaume and Weiss, George H.(1991) 'Transport Equations in Chromatography with a Finite Speed of Signal Propagation', Separation Science and Technology, 26: 2, 279 — 289
To link to this Article: DOI: 10.1080/01496399108050472
URL: http://dx.doi.org/10.1080/01496399108050472

SEPARATION SCIENCE AND TECHNOLOGY, 26(2), pp. 279–289, 1991

Transport Equations in Chromatography with a Finite Speed of Signal Propagation

JAUME MASOLIVER
DEPARTMENT DE FISICA FONAMENTAL
UNIVERSITAT DE BARCELONA
DIAGONAL 647, 08028 BARCELONA, SPAIN

GEORGE H. WEISS
NATIONAL INSTITUTES OF HEALTH
BETHESDA, MARYLAND 20892

Abstract

It is known that the diffusion equation used to model transport in a large variety of chromatographic techniques has an infinite speed of signal propagation, i.e., if $c(x,t)$ is the concentration at time t, then $c(x,t) > 0$ for any $t > 0$. We generalize and solve the telegraph equation, which is known to have a finite speed of signal propagation, to allow for asymmetric convection, as is appropriate for the theory of chromatographic processes. We derive the telegraph equation from a continuous time random walk picture and examine two sources of convection, an asymmetry in sojourn times in states in which diffusing particles move in one direction or the other, and a corresponding asymmetry in the velocities.

1. INTRODUCTION

Many mathematical analyses of the kinetics of processes related to chromatography (e.g., chromatography, electrophoresis, or centrifugation) in a homogeneous medium are based on a one-dimensional diffusion equation with a bias term exemplified by (*1*)

$$\frac{\partial c}{\partial t} = D\frac{\partial^2 c}{\partial x^2} - v\frac{\partial c}{\partial x} \tag{1}$$

In this equation $c(x,t)$ is the concentration of the assumed single component at x at time t, D is a diffusion constant, and the constant v, which represents the influence of the driving field, has the dimensions of velocity. It is well known that such an equation has an infinite propagation velocity, that is, $c(x,t) > 0$ for any $t > 0$ (2). In consequence, the solution to Eq. (1) can be regarded as being accurate only in the neighborhood of the peak $x_m = vt$. One way to derive a diffusion equation without the limitation implied by the infinite propagation velocity is to replace Eq. (1) by the so-called telegrapher's equation

$$\frac{\partial^2 c}{\partial t^2} + \frac{1}{T}\frac{\partial c}{\partial t} = u^2 \frac{\partial^2 c}{\partial x^2} \tag{2}$$

where T is a constant with the dimensions of time and u is a constant with the dimensions of velocity. This equation, however, corresponds to Eq. (1) with the parameter v set equal to 0, i.e., to a diffusion equation in the absence of a biasing field. This modified diffusion equation is known to have the property that the speed of propagation is finite rather than infinite (*2*, *3*). However, such bias is an inherent part of chromatographic processes, corresponding to the effect of the field that drives the process. In this article we propose to examine a generalization of Eq. (2) which takes into account the bias while still retaining the advantage of predicting a finite propagation velocity. Such processes have apparently not been discussed in the literature. The analysis will be based on random walks with two states (*4*), which is the basis of a recent generalization of the notion of the persistent random walk (*5*).

2. ANALYSIS

For simplicity we restrict our discussion to the one-dimensional case which is the one of major interest in applications to chromatographic processes. The basic idea defining the generalized diffusion process is that it can be in one of two states, depending on whether it is moving in the positive or negative x directions. Thus, the process consists of an alternating sequence of times during which the random walk moves in one of the two directions. The time spent in any single sojourn (i.e., the time spent moving in one or the other direction after a reversal and before the following reversal) is assumed to be a random variable characterized by a probability which we denote by $\psi_+(t)$ and $\psi_-(t)$, respectively, and

$$\Psi_+(t) = \int_t^\infty \psi_+(\tau)d\tau, \qquad \Psi_-(t) = \int_t^\infty \psi_-(\tau)d\tau \tag{3}$$

Let us assume that the initial condition for the diffusion process is $c(x,0) = \delta(x)$ and that the diffusion process takes place in an infinite medium. Further, let $f_+(x,t)$ $[f_-(x,t)]$ be the concentration at x on the assumption that the particle has moved in the positive [negative] x direction for a time t. We will also need the functions

$$h_+(x,t) = f_+(x,t)\psi_+(t), \qquad H_+(x,t) = f_+(x,t)\Psi_+(t) \tag{4}$$

similar definitions holding for motion in the negative x directions.

Since our model is one in which there are two distinguishable states, in our model we define $c_+(x,t)$ as the concentration at x at time t when the diffusing particle is moving in the positive x direction and $c_-(x,t)$ for motion in the negative x direction. Because one cannot operationally distinguish between the two concentrations, we define the observable concentration at x at time t as

$$c(x,t) = c_+(x,t) + c_-(x,t) \tag{5}$$

We will derive a partial differential equation for $c(x,t)$ that incorporates bias and therefore constitutes a generalization of Eq. (2).

There are two ways in which asymmetry can enter the theory, the first being through a difference between the two functions $f_+(x,t)$ and $f_-(x,t)$, i.e., $f_+(x,t) \neq f_-(-x,t)$, and the second is through the presumption that $\psi_+(t) \neq \psi_-(t)$. It is interesting to note that something very similar to these two possibilities occur in bacterial motion (*6*). In order to derive a partial differential equation for $c(x,t)$ valid for all $t > 0$, we will make the specific assumption that

$$f_+(x,t) = \delta(x - v_+t), \qquad \psi_+(t) = \frac{1}{T_+} \exp\left(-\frac{t}{T_+}\right) \tag{6}$$

with $f_-(x,t)$ and $\psi_-(t)$ defined similarly in terms of v_- and T_-. That is to say, motion in either direction is ballistic, and the sole source of random behavior comes from the sojourn times in the two states. An argument based on the central limit theorem suggests that provided that

$$\int_{-\infty}^{\infty} x^2 f(x,t)dx, \qquad \int_0^{\infty} t\psi(t)dt < \infty \tag{7}$$

the Gaussian concentration profile calculated from the diffusion equation will be valid at long times but not necessarily in the transient regime.

Let us denote the Fourier-Laplace transform of a generic function $g(x,t)$ by $\hat{g}(\omega,s)$ so that

$$\hat{g}(\omega,s) = \int_{-\infty}^{\infty} e^{i\omega x}dx \int_0^{\infty} e^{-st}g(x,t)dt \tag{8}$$

It has been shown that the expression for $\hat{c}(\omega,s)$ can be written (5):

$$\hat{c}(\omega,s) = \frac{[1 + \hat{h}_-(\omega,s)]H_+(\omega,s) + [1 + \hat{h}_+(\omega,s)]H_-(\omega,s)}{2[1 - \hat{h}_+(\omega,s)\hat{h}_-(\omega,s)]} \tag{9}$$

With the simple choices for the relevant functions given in Eq. (6), we can evaluate all of the functions appearing in this last equation, thereby finding

$$\begin{aligned}\hat{c}(\omega,s) &= \frac{2sT_+T_- + 2(T_+ + T_-) - i\omega T_+T_-(v_+ + v_-)}{2\{s^2T_+T_- + s(T_+ + T_-) - \omega^2 v_+v_-T_+T_- - i\omega(v_+T_+ + v_-T_-) - i\omega sT_+T_-(v_+ + v_-)\}} \\ &= \frac{s + 2\lambda - i\omega V}{s^2 + 2\lambda s - \omega^2 v_+v_- - 2i\omega\mu - 2i\omega sV}\end{aligned} \tag{10}$$

in which we have used the notation

$$2\lambda = \frac{1}{T_+} + \frac{1}{T_-}, \qquad V = \frac{v_+ + v_-}{2}, \qquad 2\mu = \left(\frac{v_+}{T_-} + \frac{v_-}{T_+}\right) \tag{11}$$

For simplicity let us consider the case in which $v_+ = -v_- = v$ or $V = 0$, so that the velocities in either directions are equal and any bias in the motion results from a tendency of particles to move for longer periods in the positive rather than the negative direction. We can derive a partial differential equation for $c(x,t)$ from the transform in Eq. (10) by using a method discussed in Ref. 5. The result of this calculation is

$$\frac{\partial^2 c}{\partial t^2} + 2\lambda\frac{\partial c}{\partial t} = v^2\frac{\partial^2 c}{\partial x^2} - 2\mu\frac{\partial c}{\partial x} \tag{12}$$

When $T_+ = T_-$, this reduces to the telegrapher's equation whose form is shown in Eq. (2), since equality of the mean residence times is equivalent to setting $\mu = 0$. Thus, in this special case the bias simply adds a term proportional to $\partial c/\partial x$ to the right-hand side, just as one does for the diffusion equation. Later we show that the case in which $v_+ \neq v_-$ can be reduced to the same form as Eq. (12) so that we are, in reality, finding a solution for the more general case even though a restriction applies on the present analysis.

Equation (12) is always reducible to an unbiased telegrapher's equation by choosing a new dependent variable $\Gamma(x,t)$ in place of $c(x,t)$ by using the transformation

$$c(x,t) = \Gamma(x,t) \exp\left[-\frac{\mu}{v^2}x - \frac{1}{2}\left(\sqrt{\frac{1}{T_+}} - \sqrt{\frac{1}{T_-}}\right)^2 t\right] \tag{13}$$

The function $\Gamma(x,t)$ therefore satisfies

$$\frac{\partial^2\Gamma}{\partial t^2} + \frac{1}{T'}\frac{\partial\Gamma}{\partial t} = v^2\frac{\partial^2\Gamma}{\partial x^2} \tag{14}$$

in which the parameter T' is defined by

$$T' = \frac{\sqrt{T_+T_-}}{2} \tag{15}$$

Since $c(x,t)$ will be assumed to obey the initial conditions

$$c(x,0) = c_0\delta(x), \qquad \left.\frac{\partial c}{\partial t}\right|_{t=0} = 0 \tag{16}$$

the function $\Gamma(x,t)$ must be found from the solution to Eq. (14) subject to the same set of initial conditions, i.e., $\Gamma(x,0) = c_0\delta(x)$ and $\partial\Gamma/\partial t|_{t=0} = 0$. The simplest way to solve Eq. (14) is to once again take its Fourier-Laplace transform, which can be expressed as

$$\hat{\Gamma}(\omega,s) = \frac{c_0}{v^2}\left(s + \frac{1}{T'}\right)\frac{1}{\omega^2 + \dfrac{s^2}{v^2} + \dfrac{s}{v^2T'}} \tag{17}$$

Let $\bar{\Gamma}(x,s)$ denote the Laplace transform of $\Gamma(x,t)$, or correspondingly the inverse Fourier transform of Eq. (17). One readily finds this transform to be

$$\bar{\Gamma}(x,s) = \frac{c_0}{2v}\left(s + \frac{1}{T'}\right)\frac{1}{\sqrt{s^2 + \frac{s}{T'}}}\exp\left[-\frac{|x|}{v}\sqrt{s^2 + \frac{s}{T'}}\right] \tag{18}$$

Let $f(t)$ be the inverse transform of the function

$$\hat{f}(s) = \frac{1}{\sqrt{s^2 + \frac{s}{T'}}}\exp\left[-\frac{|x|}{v}\sqrt{s^2 + \frac{s}{T'}}\right] \tag{19}$$

which is found to equal (7)

$$f(t) = \exp\left(-\frac{t}{2T'}\right) I_0\left[\frac{1}{2vT'}\sqrt{v^2t^2 - x^2}\right] H\left(t - \frac{|x|}{v}\right) \tag{20}$$

in which $I_0(x)$ is a Bessel function of imaginary argument, and $H(x)$ is the Heaviside step function, i.e., $H(x) = 0$ when $x < 0$, $= 1$ when $x > 0$ and $H(0) = 1/2$. The combination of Eqs. (18)–(20) shows that $\Gamma(x,t)$ can be represented in terms of $f(t)$ as

$$\begin{aligned}\Gamma(x,t) &= \frac{c_0}{2vT'}\left(f(t) + T'\frac{df(t)}{dt}\right)\\ &= \frac{c_0}{2vT'}\left(H\left(t - \frac{|x|}{v}\right)\left[1 + T'\frac{d}{dt}\right]\exp\left(-\frac{t}{2T'}\right)I_0\right.\\ &\quad\times\left.\left[\frac{1}{2vT'}\sqrt{v^2t^2 - x^2}\right] + \exp\left(-\frac{t}{2T'}\right)\delta\left(t - \frac{|x|}{v}\right)\right),\\ &\quad t > 0\end{aligned} \tag{21}$$

where $\delta(x)$ is a Dirac delta function. The term containing the delta function gives the contribution from the ballistic motion of those particles that have always moved in the same direction. The delta function contribute to $\Gamma(x,t)$ disappears rapidly compared to the contribution from the first set of terms.

Because of the Heaviside step function in Eq. (21), it is evident that $c(x,t)$ must vanish for all x that satisfy $x^2 > (vt)^2$. This is to be contrasted to the solution of the diffusion equation which is nonnegative for all $t > 0$. In Fig. 1 we show some typical concentration profiles calculated from Eq. (13), omitting the delta function term. The increasing asymmetry of these concentration profiles as the time increases is evident from the figure, as well the sharp cutoffs at the endpoints $x = \pm vt$. We have not included the delta function peaks at the endpoints.

At sufficiently long times $c(x,t)$ will indeed approach the shifted Gaussian form predicted by the solution to a diffusion equation. This is evident from the behavior of $\hat{c}(\omega,s)$ in the limit $s \to 0$ where the term proportional to s^2 in the denominator is negligible in comparison to s and the term in s in

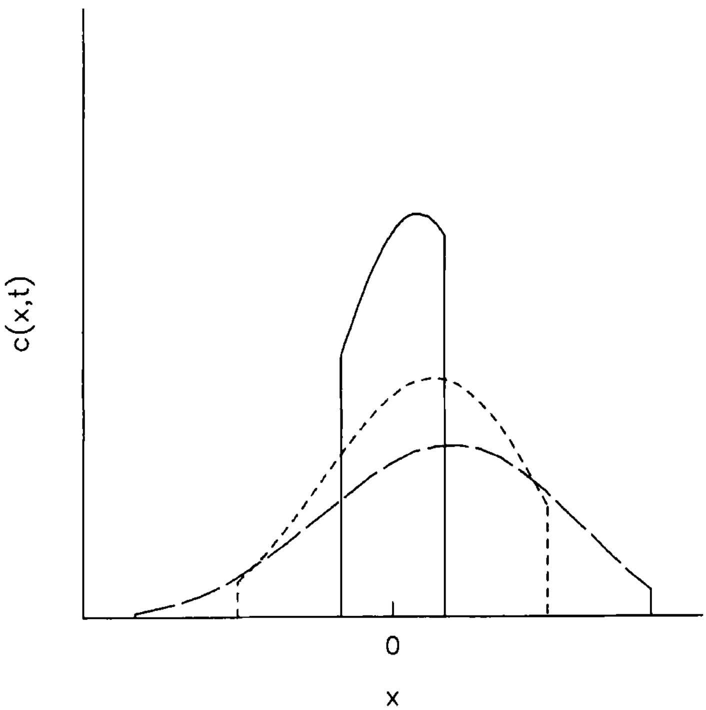

FIG. 1. Curves of the concentration profile $c(x,t)$ plotted from Eq. (13) for the values $c_0 = 1$, $v = 1$, $T_+ = 8$, $T_- = 2$ for increasing values of time: (——) $t = 1$; (- - -) $t = 3$; (– – –) $t = 5$. The delta functions at the endpoints are not included in the figure. At very short times the concentration profiles differ considerably from the shifted Gaussian expected on the basis of a biased diffusion equation.

the numerator can be neglected with respect to 2λ. In this regime we find

$$\hat{c}(\omega,s) \approx \frac{2\lambda c_0}{2\lambda s + 2i\mu\omega + v^2\omega^2} \tag{22}$$

whose inverse is readily found by first inverting the Laplace transform followed by an inversion of the Fourier transform. The result is

$$c(x,t) \approx \frac{c_0}{v}\sqrt{\frac{\lambda}{2\pi t}}\exp\left[-\frac{\lambda}{2v^2 t}\left(x + \frac{\mu t}{\lambda}\right)^2\right] \tag{23}$$

which is the desired Gaussian. One way of assessing the time range over which one must correct the diffusion approximation is to examine the time-dependence of the average displacement at time t, which is defined by

$$\langle x(t)\rangle \equiv \int_0^\infty x\,\frac{c(x,t)}{c_0}\,dx = -i\,\frac{1}{c_0}\,\frac{\partial\hat{c}}{\partial\omega}\bigg|_{\omega=0} \tag{24}$$

When the peak is a Gaussian, as would be found for a diffusion model, $\langle x(t)\rangle$ is proportional to t for all values of the time, as one indeed finds from the approximate expression in Eq. (23). On returning to Eq. (10) and calculating the derivative indicated in Eq. (24), one finds, by a Tauberian argument for Laplace transforms (*8*), that the first two terms in the expansion of the long time behavior of $\langle x(t)\rangle$ are

$$\langle x(t)\rangle \approx \frac{1}{4\lambda}\left(t - \frac{1}{\lambda}\right) \tag{25}$$

which suggests that the time scale for which the diffusion approximation is useful is specified by $t \gg \lambda^{-1}$ or

$$\left(\frac{1}{T_+} + \frac{1}{T_-}\right)\frac{t}{2} \gg 1 \tag{26}$$

To this point we have examined the situation in which the velocities are equal and opposite for the two states but the average sojourn times are unequal. When the velocities as well as the average residence times are also allowed to differ, we get a slightly more complicated form from $\hat{c}(\omega,s)$ as indicated by the presence of a term proportional to ωs in the denominator of Eq. (10). This transform is also equivalent to a partial differential equation for $c(x,t)$ which is

$$\frac{\partial^2 c}{\partial t^2} + 2\lambda \frac{\partial c}{\partial t} + 2V \frac{\partial^2 c}{\partial x \partial t} = \bar{v}^2 \frac{\partial^2 c}{\partial x^2} - 2\mu \frac{\partial c}{\partial x} \qquad (27)$$

where we have set $\bar{v}^2 = -v_+ v_-$. This equation can be reduced in form to the earlier shifted telegrapher's equation in Eq. (14) by eliminating the mixed derivative through the introduction of a new running coordinate, ξ, defined as

$$\xi = x - Vt \qquad (28)$$

which transforms Eq. (27) into

$$\frac{\partial^2 c}{\partial t^2} + 2\lambda \frac{\partial c}{\partial t} = (V^2 + \bar{v}^2) \frac{\partial c^2}{\partial \xi^2} - 2(\mu - \lambda V) \frac{\partial c}{\partial \xi}$$

$$= \frac{1}{4} (v_+ - v_-)^2 \frac{\partial c^2}{\partial \xi^2} - \frac{(v_- - v_+)}{2} \left(\frac{1}{T_+} - \frac{1}{T_-} \right) \frac{\partial c}{\partial \xi} \qquad (29)$$

This equation reduces to the earlier shifted telegrapher's equation in Eq. (12) when v_+ is set equal to $-v_-$. Since when $t = 0$, $\xi = x$, it follows that Eq. (29) is to be solved subject to the initial conditions

$$c(\xi,0) = c_0 \delta(\xi), \qquad \partial c(\xi,t)/\partial t|_{t=0} = 0 \qquad (30)$$

Our analysis of Eq. (12) can be repeated with the variable x in that equation replaced by ξ in Eq. (29). We can conclude from our earlier analysis that the concentration profiles have compact support, being identically equal to zero for $\xi^2 > (vt)^2$. A second conclusion that results from our earlier analysis is that the concentration profile $c(\xi,t)$ is asymptotically a Gaussian centered at the moving point $x = Vt$. In the class of models represented by the assumptions in Eq. (6), the simpler diffusion approach yields satisfactory results in the neighborhood of the peak but does not reproduce the behavior in the tails very well.

A natural generalization of all our analysis allows for more general forms of the functions $h_+(x,t)$ and $h_-(x,t)$ than those given in Eq. (6). We mention some of the features expected in such models, without giving any details of the analysis. When the two moments $\int_0^\infty dt \int_{-\infty}^\infty x^2 h(x,t) dx$ and $\int_{-\infty}^\infty dx \int_0^\infty t h(x,t) dt$ are finite, the asymptotic concentration profile will be a

Gaussian, as one finds from an argument based on the analysis of Eq. (9) in the limits $s,\omega \to 0$. In such cases the generalized diffusion equation may become too complicated to form a useful starting point for any analysis. For example, if one changes the assumption of ballistic motion to biased diffusion so that the $f(x,t)$ in Eq. (6) are replaced by

$$\begin{aligned} f_+(x,t) &= (4\pi Dt)^{-1/2} \exp[-(x - vt)^2/(4Dt)] \\ f_-(x,t) &= (4\pi Dt)^{-1/2} \exp[-(x + vt)^2/(4Dt)] \end{aligned} \tag{31}$$

the sojourn time densities remaining of negative exponential form as in Eq. (6) with $T_+ = T_-$, it is possible to derive a generalized diffusion equation of the form

$$\frac{\partial^2 c}{\partial t^2} + \frac{2}{T}\frac{\partial c}{\partial t} = \left(v^2 + 2\frac{D}{T}\right)\frac{\partial^2 c}{\partial x^2} + 2D\frac{\partial^3 c}{\partial x^2 \partial t} - D^2\frac{\partial^4 c}{\partial x^4} \tag{32}$$

However, the analysis of such equations is obviously quite complicated. It is clear that since the expressions for $f_+(x,t)$ and $f_-(x,t)$ given in Eq. (31) allow for an infinite speed of signal propagation, solutions to Eq. (32) will have this property as well. Thus we can attribute the fact that the solution to Eq. (12) has compact support to the assumption of ballistic motion contained in Eq. (6).

As a final comment, we note that if either of the moments $\int_0^\infty dt \int_{-\infty}^\infty x^2 h(x,t)dx$ or $\int_{-\infty}^\infty dx \int_0^\infty t h(x,t)dt$ is infinite, one can expect that the peaks in the concentration profile will show enhanced asymmetry and will not approach a Gaussian shape asymptotically, much as is suggested in Refs. *9* and *10*.

Acknowledgments

J.M. gratefully acknowledges partial support by the Comision Interministerial de Ciencia y Tecnologia (CICYT) under contract PS87-0046 and by the Societat Catalana de Fisica (Institut Estudis Catalans). G.H.W. thanks the Department of Fundamental Physics, University of Barcelona, for its very generous hospitality during the time that this work was in progress.

REFERENCES

1. J. C. Giddings, *Dynamics of Chromatography. Part 1. Principles and Theory,* Dekker, New York, 1965.

2. P. M. Morse and H. Feshbach, *Methods of Theoretical Physics,* Vol. 1, McGraw-Hill, New York, 1953.

3. D. D. Joseph and G. Preziosi, "Heat Waves," *Rev. Mod. Phys.*, *61*, 41–73 (1989).
4. G. H. Weiss, "The Two-State Random Walk," *J. Stat. Phys.*, *15*, 157–165 (1976).
5. J. Masoliver, K. Lindenberg, and G. H. Weiss, "A Continuous-Time Generalization of the Persistent Random Walk," *Physica A*, pp. 891–898 (1989).
6. R. Nossal, "Stochastic Aspects of Biological Locomotion," *J. Stat. Phys.*, *30*, 391–400 (1983).
7. G. E. Roberts and H. Kaufman, *Table of Laplace Transforms*, Saunders, Philadelphia, 1966.
8. G. Doetsch, *Theorie und Anwendung der Laplace-Transformation*, Dover (reprint), New York, 1943.
9. G. H. Weiss, "Chromatographic Kinetics and the Phenomenon of Tailing," *Sep. Sci. Technol.*, *17*, 1101–1115 (1982).
10. G. H. Weiss, "On a Generalized Transport for Chromatographic Systems," in *Transport and Relaxation in Random Materials* (J. Klafter, R. J. Rubin, and M. F. Shlesinger, eds.), World Scientific, Singapore, 1986, pp. 394–406.

Received by editor March 13, 1990