Dispersion in Laminar Flow in Short Tubes

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The axial dispersion of an impulse of tracer injected into a fluid in laminar flow in a tube is caused by the interaction of radial diffusion and the nonuniform velocity profile. Taylor (1953) and Aris (1956) showed that dispersion of the solute leads to a Gaussian area-average concentration profile sufficiently far downstream. The process can thus be described by a Fickian mechanism, with the dispersion coefficient, ϵ, related to the molecular diffusivity, $\mathcal{D}$, by

$$\frac{\epsilon}{\mathcal{D}} = 1 + \frac{Pe^2}{192} \tag{1}$$

where $Pe = Ua/\mathcal{D}$ is a Péclet number, with U the centerline velocity and a the tube radius. Applicability of this result requires a tube length $L \gg Ua^2/2\mathcal{D}$, and the course of dispersion in tubes much shorter than this is much more complicated than suggested by Eq. 1. Describing this evolution of concentration profiles to the Taylor-Aris limit has been the subject of a large number of studies employing numerical and analytical approaches, or some combination, as reviewed recently by Vrentas and Vrentas (1988).

For determining radially averaged concentration profiles under the frequently encountered conditions of short times or large Péclet numbers, Yu's (1976, 1979, 1981) method is, as noted by Vrentas and Vrentas, the most useful. Yu's approach is to expand the local solute concentration radially in a series of Bessel functions and then to solve the resulting series of partial differential equations in the axial coordinate and time by Fourier and Laplace transformation, respectively. Although truncation of the radial series allows some economy in computing the solution, the Fourier transformation can be extremely expensive. This is especially true at very short times, where the extent of axial spreading is small and it is thus necessary to include very high frequencies in the transformation. The method of DeGance and Johns (1978a, b, 1980) suffers from a similar problem: their axial expansion, in terms of Hermite polynomials, also applies to an infinite domain.

This paper describes a modification of Yu's method which leads to an appreciable improvement in computational efficiency. It treats the infinite *Pe* limit, for which it makes use of a Fourier series expansion axially instead of Fourier transformation. This is possible because of the absence of the axial diffusion term, as a result of which axial transport is purely convective and the axial domain is therefore finite. There is no loss of generality in the restriction to infinite *Pe* since solutions for all other *Pe* can be easily obtained by a Gaussian smoothing of the infinite *Pe* solution (Wang and Stewart, 1983). The solution scheme can also be adapted, following the approaches described by DeGance and Johns (1978a, b), to obtain solutions for systems of different cross-section or with different velocity profiles, as well as for the situation in which there is first-order reaction at the walls.

Problem Statement

We consider fully developed laminar flow in a tube for which the local solute concentration, $C(\zeta, \xi, \tau)$, satisfies the scaled convection diffusion equation in the absence of axial diffusion,

$$\frac{\partial C}{\partial \tau} = \frac{1}{\xi}\frac{\partial}{\partial \xi}\left(\xi \frac{\partial C}{\partial \xi}\right) - \left(\frac{1}{2} - \xi^2\right)\frac{\partial C}{\partial \zeta}. \tag{2}$$

The dimensionless variables and parameters are defined as

$$\xi = \frac{r}{a} \quad \tau = \frac{\mathcal{D}t}{a^2} \quad \zeta = \frac{z\mathcal{D}}{Ua^2} - \frac{\tau}{2}, \tag{3}$$

where z, r and t are the axial and radial coordinates and time, respectively. Eq. 2 is to be solved subject to the boundary conditions

$$\frac{\partial C}{\partial \xi} = 0 \quad \text{at} \quad \xi = 0, 1, \tag{4}$$

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implying symmetry at the centerline and no flux at the walls, and the initial condition

$$C = \delta(\zeta) \quad \text{at} \quad \tau = 0. \tag{5}$$

Solution Procedure

The local solute concentration, $C(\zeta, \xi, \tau)$, is found by a method similar to those of Yu (1976, 1979, 1981) and DeGance and Johns (1978b). It is expanded in axial and radial series, with the axial expansion a Fourier series over the finite domain into which solute will be transported up to any given time of interest, τ_0. This domain is $\zeta \in (-\tau_0/2, \tau_0/2)$, with τ_0 simply a parameter used in the computations. This restriction of the axial domain to the actual region accessible to solute is the main reason for the computational economy of the procedure. Results for a given τ can actually be obtained using any value of $\tau_0 > \tau$, but the greatest efficiency will be for $\tau_0 = \tau$. Thus

$$C(\zeta, \xi, \tau) = \sum_{n=-\infty}^{\infty} a_n(\xi, \tau) e^{(i2n\pi\zeta/\tau_0)}, \tag{6}$$

which yields a set of partial differential equations for the complex coefficients, $a_n(\xi, \tau)$ (note that a_{-n} is the complex conjugate of a_n since C is real):

$$\frac{\partial a_n}{\partial \tau} = \frac{1}{\xi}\frac{\partial}{\partial \xi}\left(\xi \frac{\partial a_n}{\partial \xi}\right) - \left(\frac{1}{2} - \xi^2\right)\frac{i2n\pi a_n}{\tau_0}. \tag{7}$$

These equations are to be solved subject to the radial boundary conditions, Eq. 4, and the initial conditions

$$a_n = \frac{1}{\tau_0} \quad \text{at} \quad \tau = 0. \tag{8}$$

The coefficients, like those of Yu (1976, 1979, 1981) and DeGance and Johns (1978b), are expanded radially in terms of the radial Eigenfunctions

$$\psi_l(\xi) = \frac{J_0(\lambda_l \xi)}{|J_0(\lambda_l)|} \tag{9}$$

where

$$\{\lambda_l\} = \{\lambda \geq 0 | J_1(\lambda) = 0\}. \tag{10}$$

Thus

$$a_n = \sum_{l=0}^{\infty} < a_n, \psi_l(\xi) > \psi_l(\xi) \equiv \sum_{l=0}^{\infty} a_{n,l}\psi_l(\xi) \tag{11}$$

where

$$\langle ., . \rangle = 2\int_0^1 .. \, \xi \, d\xi, \tag{12}$$

and substitution in Eq. 7 yields a set of ordinary differential equations for the $a_{n,l}$'s:

$$\frac{da_{n,l}}{d\tau} = -\lambda_l^2 a_{n,l} - \frac{i4\pi n}{\tau_0}\sum_{k=0}^{\infty} a_{n,k}A_{k,l} \quad l = 0, 1, 2, \ldots, \infty \tag{13}$$

where

$$A_{k,l} = \int_0^1 \left(\frac{1}{2} - \xi^2\right)\xi\psi_k\psi_l \, d\xi. \tag{14}$$

The initial conditions for the $a_{n,l}$ are

$$a_{n,0}(0) = \frac{1}{\tau_0} \quad n = -\infty, \ldots, \infty \tag{15}$$

with all other $a_{n,l}(0)$ being zero.

The coefficients described by Eq. 13 can solved for independently for each value of n. For $n = 0$ the solution is simply

$$a_{0,l} = a_{0,l}(0)e^{-\lambda_l^2\tau} \quad l = 0, 1, 2, \ldots, \tag{16}$$

but for other n the equations are coupled and the infinite series must be truncated to make a simultaneous solution possible. The procedure is best followed by writing Eq. 13 for each n in matrix form as

$$\frac{d\boldsymbol{a}}{d\tau} = \boldsymbol{P}\boldsymbol{a}, \tag{17}$$

with $\boldsymbol{a}$ and $\boldsymbol{P}$ infinite-dimensional for the moment. As was done by Yu (1976, 1979, 1981), the fast and slow modes are treated separately; here this amounts to partitioning $\boldsymbol{a}$ into $\boldsymbol{a}_s = [a_{n,1}, a_{n,2}, \ldots, a_{n,M}]$ and $\boldsymbol{a}_f = [a_{n,M+1}, a_{n,M+2}, \ldots, a_{n,N}]$ with $\boldsymbol{a}$ truncated at some large N. $\boldsymbol{P}$ is partitioned similarly, from which the coupled equations

$$\frac{d\boldsymbol{a}_s}{d\tau} = \boldsymbol{P}_{ss}\boldsymbol{a}_s + \boldsymbol{P}_{sf}\boldsymbol{a}_f \tag{18}$$

$$\frac{d\boldsymbol{a}_f}{d\tau} = \boldsymbol{P}_{fs}\boldsymbol{a}_s + \boldsymbol{P}_{ff}\boldsymbol{a}_f \tag{19}$$

are obtained. For

$$\tau \gg 1/Re(\mu_{ff}^+), \tag{20}$$

pseudo-steady-state can be assumed for Eq. 19, from which $\boldsymbol{a}_f$ can be solved algebraically as

$$\boldsymbol{a}_f = -\boldsymbol{P}_{ff}^{-1}\boldsymbol{P}_{fs}\boldsymbol{a}_s \tag{21}$$

with Eq. 18 then giving

$$\boldsymbol{a}_s = e^{(\boldsymbol{P}_{ss} - \boldsymbol{P}_{sf}\boldsymbol{P}_{ff}^{-1}\boldsymbol{P}_{fs})\tau}\boldsymbol{a}_s(0). \tag{22}$$

Numerical implementation is straightforward, and standard routines were used for most steps. Matrix exponentials were computed by scaling and squaring with an (8, 8) Padé approximant (Moler and van Loan, 1978). Convergence of the truncated axial series is assured by the Riemann-Lebesgue lemma (Haberman, 1983), but values for M and N are needed in addition to the number of axial terms to include in the expansion, Eq. 6. M should be large enough for Inequality 20 to be satisfied, with a bound on the Eigenvalue μ_{ff}^+ obtainable by Gershgorin's theorem (Wilkinson, 1965): the Eigenvalues μ_{ff} are within

$(4\pi n/\tau_0)\ \Sigma_{i=M+1}^{N} |A_{kj}|$ of the diagonal elements $-\lambda_i^2$ of P_{ff}. Second-order perturbation estimates for small n (Wilkinson, 1965) as well as actual computed values for all n show that $-\lambda_{M+1}^2$ is, in fact, a conservative estimate of the dominant eigenvalue, μ_{ff}^+, allowing a reasonable M to be chosen for each n. A suitable value of N can be estimated by noting the effect of increasing N on elements of the matrix in the exponent in Eq. 22. This can be done by the bordering method (Faddeev and Faddeeva, 1963), and economical approaches to computing the effect on the matrix exponential are also available. However, N has a much smaller effect on the results than does M, and Eq. 21 is much cheaper computationally than Eq. 22, so a major effort to optimize N is unwarranted. Since the axial terms can be treated independently, the effect of adding additional terms in the expansion, Eq. 6, can be seen directly.

Although the above procedure provides local concentrations, C, in principle, it is usually some average concentration that is of interest. Quadrature turns the ψ_k functions into algebraic weights. The area-average concentration is particularly simple, since only the trivial Eigenfunction, $\psi_0 = 1$, gives rise to a nonzero contribution, and hence only the $a_{n,0}$ coefficients are needed. However, other transverse averages, e.g., the cup-mixing average, can be found with little additional effort.

Results and Discussion

Results are presented separately in terms of the area-average concentration, the most widely used average for previous calculations of this kind, and the cup-mixing concentration. The profiles were obtained by first creating concentration surfaces plotted against time and axial position, as shown for the area-average in Figure 1. The axial position coordinate is scaled with time consistent with the domain of the Fourier series expansion. The surfaces were obtained by solving the convective diffusion equation for a set of τ_0 values and using a two-dimensional polynomial interpolation on the concentration field. As expected, the expansions needed became smaller at longer times. For example, satisfactory results at $\tau = 0.005$ can be obtained with $M = 50$, $N = 75$, and 400 axial terms, while at $\tau = 0.02$ $M = 11$, $N = 35$, and 200 axial terms are adequate. These two responses required about 32 hours and 12 minutes of CPU time, respectively, on a Sun 4/110. Smaller times than those presented are accessible by using larger expansions, but Lighthill's (1966)

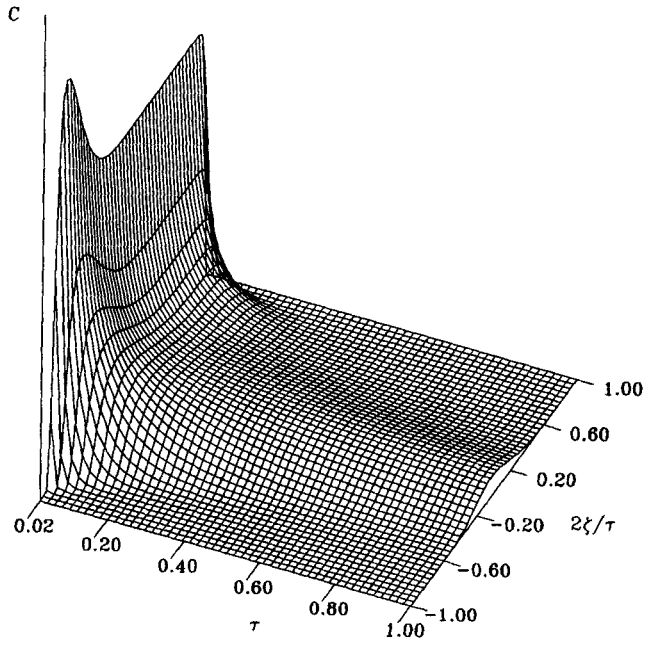

Figure 1. Area-average concentration surface.

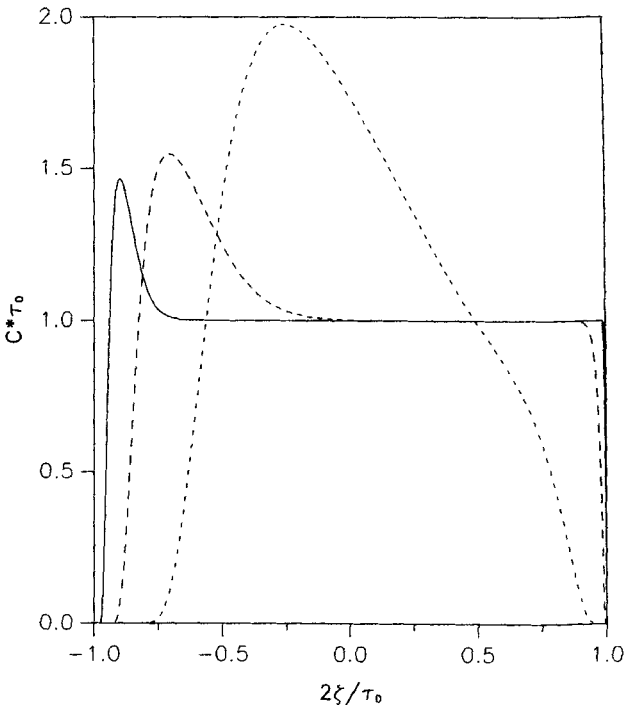

Figure 2. Area-average axial concentration profiles.
τ values: —, 0.002; —, 0.02; ---, 0.2

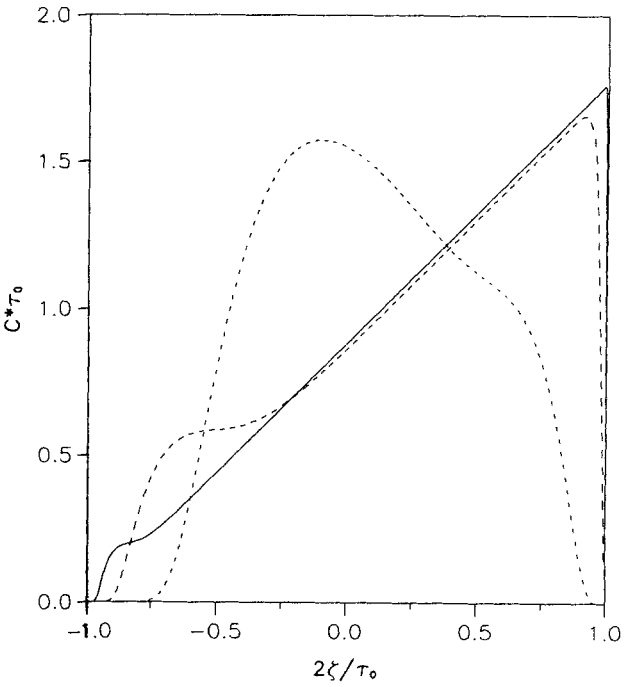

Figure 3. Cup-mixing average axial concentration profiles.
τ values: —, 0.002; —, 0.02; ---, 0.2

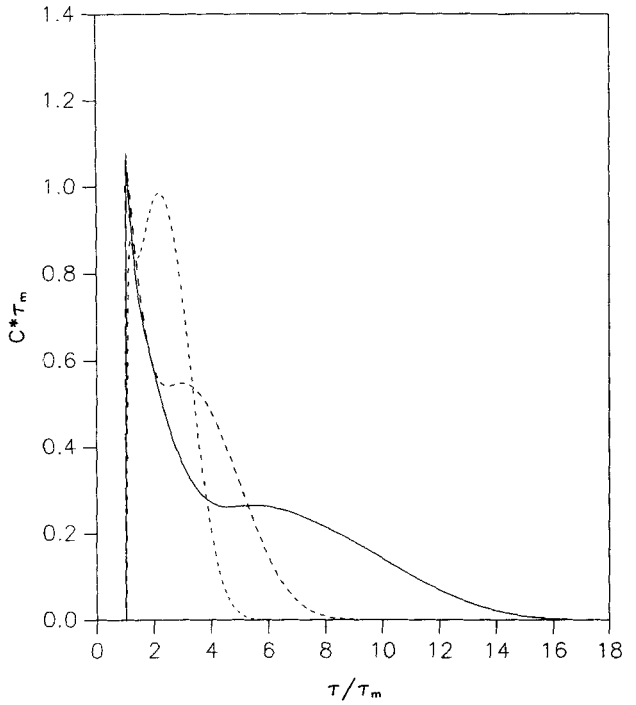

Figure 4. Area-average exit concentration profiles.
τ_m values: —, 0.002; --, 0.02; ---, 0.1

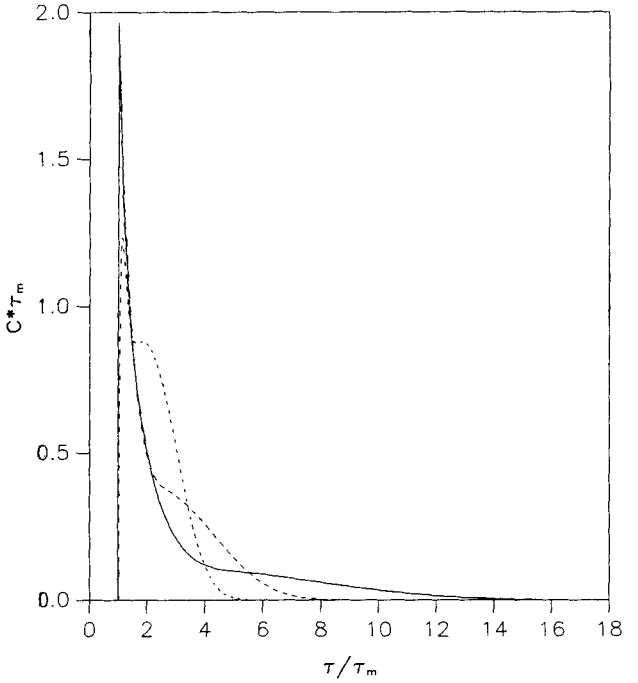

Figure 5. Cup-mixing average exit concentration profiles.
τ_m values: —, 0.002; --, 0.02; ---, 0.1

treatment of radial diffusion around the "snout" is more economical at very short times.

Instantaneous axial concentration profiles are found from the surface along lines of constant τ, while concentration profiles at fixed positions as a function of time are along curves in the $\tau - 2\zeta/\tau$ plane. Area-average and cup-mixing axial profiles for several values of τ are shown in Figures 2 and 3. The last two values of τ were chosen to correspond to values for which area-average concentrations were presented by Yu (1981); the agreement is excellent, with comparable performance using Yu's method requiring between one and two orders of magnitude more CPU time than the present one. The profiles are asymmetric because of the interaction of axial convection and radial diffusion. The leading edge at short times corresponds to purely convective transport (Taylor, 1953) while radial diffusion can be accounted for in the early stages as described by Lighthill (1966).

Figures 4 and 5 show area-average and cup-mixing average exit concentration profiles as functions of time for tubes of various lengths, characterized by the minimum transit time, τ_m. The results agree qualitatively with the numerical results of Mayock et al. (1980), Atwood and Golay (1981), and Gill and Ananthakrishnan (1967) in predicting double peaks in the area-average profiles, which result from the segregation of solute into the faster-moving region near the center and the slower-moving region near the wall. Our results do not agree exactly with those of other groups, the most likely source of the discrepancies being the inaccuracy of finite-difference methods in coping with the steep gradients present at short times; errors are also cumulative in finite-difference solutions. The double-peaked elution profiles have been used as a method for estimating molecular weights (Kelleher and Trumbore, 1984; Trumbore et al., 1985); the cup-mixing results are probably the relevant ones for the experimental set-up used there, in view of the mixing likely at the entrance to the detector used.

Surfaces such as that shown in Figure 1 need to be calculated only once, and can then be used to obtain results for any value of *Pe* through the use of Gaussian smoothing (Wang and Stewart, 1983). Since this technique applies to the local concentration, it also applies to all transverse averages.

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Notation

a = tube radius
a_n = Fourier coefficient
$a_{n,l}$ = Fourier-Bessel coefficient
$\boldsymbol{a}$ = vector of $a_{n,l}$'s for given n
$A_{k,l}$ = constants defined by Eq. 14
C = local solute concentration
$\mathcal{D}$ = binary diffusivity
L = tube length
M = limit of slow mode expansion
N = limit of fast mode expansion
$\boldsymbol{P}$ = matrix defined by Eq. 17
Pe = Péclet number, $Ua/\mathcal{D}$
r = radial coordinate
t = time
U = centerline velocity
z = axial coordinate

Greek letters

ϵ = dispersion coefficient
ζ = dimensionless axial coordinate, $z\mathcal{D}/Ua^2 - \tau/2$
λ_i = radial Eigenvalue
μ_{ff} = Eigenvalue of $\boldsymbol{P}_{ff}$

μ_{ff}^{+} = largest Eigenvalue of P_{ff}
ξ = dimensionless radial coordinate, r/a
τ = dimensionless time, $\mathcal{D}t/a^2$
τ_m = dimensionless minimum transit time, $\mathcal{D}L/Ua^2$
τ_0 = upper limit of τ
ψ = radial Eigenfunction

Subscripts

f = fast
l = Bessel mode
n = Fourier mode
s = slow

Literature Cited

Aris, R., "On the Dispersion of a Solute in a Fluid Flowing through a Tube," *Proc. Roy. Soc. A*, **235**, 67 (1956).

Atwood, J. G., and M. J. E. Golay, "Dispersion of Peaks by Short Straight Open Tubes in Chromatographic Systems," *J. Chrom.*, **218**, 97 (1981).

De Gance, A. E., and L. E. Johns, "The Theory of Dispersion of Chemically Active Solutes in a Rectilinear Flow Field," *Appl. Sci. Res.*, **34**, 189 (1978a).

———, "On the Dispersion Coefficients for Poiseuille Flow in a Circular Cylinder," *Appl. Sci. Res.*, **34**, 227 (1978b).

———, "On the Construction of Dispersion Approximations to the Solution of the Convective Diffusion Equation," *AIChE J.*, **26**, 411 (1980).

Faddeev, D. K., and V. N. Faddeeva, *Computational Methods of Linear Algebra*, W. H. Freeman and Company, San Francisco (1963).

Gill, W. N., and V. Ananthakrishnan, "Laminar Dispersion in Capillaries: The Slug Stimulus, " *AIChE J.*, **13**, 801 (1967).

Haberman, R., *Elementary Applied Partial Differential Equations*, Prentice-Hall, Englewood Cliffs (1983).

Kelleher, F. M., and C. N. Trumbore, "Dispersion of Protein Solutions in Short, Open Capillary Tubes as a Method for Rapid Molecular Weight Determination," *Anal. Biochem.*, **137**, 20 (1984).

Lighthill, M. J., "Initial Development of Diffusion in Poiseuille Flow," *J. Inst. Maths. Applics.*, **2**, 97 (1966).

Mayock, K. P., J. M. Tarbell, and J. L. Duda, "Numerical Simulation of Solute Dispersion in Laminar Tube Flow," *Sep. Sci. Tech.*, **15**, 1285 (1980).

Moler, C., and C. van Loan, "Nineteen Dubious Ways to Compute the Exponential of a Matrix," *SIAM Rev.*, **20**, 801 (1978).

Taylor G., "Dispersion of Soluble Matter in Solvent Flowing Slowly Through a Tube," *Proc. Roy. Soc. A*, **317**, 186 (1953).

Trumbore, C. N., M. Grehlinger, M. Stowe, and F. M. Kelleher, "Further Experiments on a New, Fast Method for Determining Molecular Weights of Diffusing Species in a Liquid Phase," *J. Chrom.*, **322**, 443 (1985).

Vrentas, J. S., and C. M. Vrentas, "Dispersion in Laminar Tube Flow at Low Peclet Numbers or Short Times," *AIChE J.*, **34**, 1423 (1988).

Wang, J. C., and W. E. Stewart, "New Descriptions of Dispersion in Flow Through Tubes: Convolution and Collocation Methods," *AIChE J.*, **29**, 493 (1983).

Wilkinson, J. H., *The Algebraic Eigenvalue Problem*, Oxford University Press, Oxford (1965).

Yu, J. S., "An Approximate Analysis of Laminar Dispersion in Circular Tubes," *ASME J. Appl. Mech.*, **43**, 537 (1976).

———, "On Laminar Dispersion for Flow Through Round Tubes," *ASME J. Appl. Mech.*, **46**, 750 (1979).

———, "Dispersion in Laminar Flow Through Tubes by Simultaneous Diffusion and Convection," *ASME J. Appl. Mech.*, **48**, 217 (1981).

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