Wave Model for Longitudinal Dispersion: Development of the Model

K. R. Westerterp, V. V. Dil'man, and A. E. Kronberg
Chemical Reaction Engineering Laboratories, Dept. of Chemical Engineering, Twente University of Technology,
7500 AE Enschede, The Netherlands

A new 1-D model for longitudinal dispersion is proposed as an alternative to the Fickian-type dispersed plug-flow model. Accounting for significant features of longitudinal mixing gives rise to a quasilinear hyperbolic system of two first-order equations for the average concentration and the dispersion flux instead of one second-order parabolic equation for the average concentration. The model equations are obtained based on minor extensions of the heuristic equilibrium analysis of Taylor. A qualitative, more general derivation of the equations is given on the basis of a simple generalization of Fick's law, taking into account the finite velocity of fluid elements. For linear problems the mean concentration and the dispersion flux obey a hyperbolic equation of the second order. The proposed hyperbolic model contains three parameters that depend only on the flow conditions, the physical properties of the fluid, and the geometry of the system. It effectively resolves the well-known problem of boundary conditions that, for unidirectional flow, are formulated now only at the reactor inlet. The new model eliminates the conceptual shortcomings inherent to the Fickian dispersed plug-flow model: it predicts a finite velocity of signal propagation and does not involve backmixing in the case of unidirectional flow.

Introduction

Most convective heat and mass dispersion phenomena strongly resemble molecular diffusion, only they have absolutely different time, velocity, and space scales. The relationship of these scales to other process scales may be completely different than for molecular diffusion. Therefore application of Fick's law of diffusion to describe convective dispersion phenomena often is not justified and leads to erroneous results. Longitudinal dispersion due to flow nonuniformities of different scales is just such a case.

Classical dispersion model

The commonly encountered model of contactors and chemical reactors is the longitudinal-dispersed plug-flow or simply longitudinal-dispersion model. For one-phase flow the model equation is usually written as

$$\frac{\partial \bar{c}}{\partial t} + \bar{u}\frac{\partial \bar{c}}{\partial x} + q(\bar{c}, x, t) = D_e \frac{\partial^2 \bar{c}}{\partial x^2} \qquad (1)$$

with the well-known boundary conditions after Danckwerts (1953):

$$x = 0, \quad \bar{u}\bar{c}_0 = \bar{u}\bar{c} - D_e \frac{\partial \bar{c}}{\partial x}; \qquad x = L, \quad \frac{\partial \bar{c}}{\partial x} = 0. \qquad (2)$$

For multicomponent or multiphase systems the same equations and boundary conditions are used for each particular component in every phase. So the dispersion model of Eqs. 1 and 2 accounts for all the factors causing different residence times by means of a constant effective longitudinal dispersion coefficient D_e (Westerterp et al., 1987). Usually this coefficient is to be determined experimentally for the system of interest, especially from pulse signals through nonreactive systems. For simple cases such as well-developed, laminar, or turbulent flows in tubes, where the Taylor-Aris dispersion is

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Correspondence concerning this article should be addressed to K. R. Westerterp.
Permanent address of V. V. Dil'man: Kurnakov Institute of General and Inorganic Chemistry of Russian Academy of Sciences, Leninsky Prospect 31, Moscow 117907, Russia.

the main mechanism of axial mixing, the longitudinal dispersion coefficient can be easily calculated. Since the model characterizes the longitudinal mixing by only one single parameter D_e, its simplicity has made it the most widely used general model for nonideal flow through a system. This model also benefits from its analogy with the diffusion equation and the possibility of utilizing all classical mathematical solutions available for diffusion problems. It is the most common model also because the information required to describe velocity profiles and transverse mixing in reactors is usually not available. We will further call this model of Eqs. 1 and 2 the "standard dispersion model" (SDM).

The SDM has been extensively used to describe the performance of single- and multiphase systems; see Wen and Fan (1975), Shah et al. (1978), Westerterp et al. (1987), and Froment and Bischoff (1990). However, the main assumption underlying the dispersion model of Eqs. 1 and 2—all mixing processes in the longitudinal direction follow a Fick's law type of diffusion equation regardless of the actual mechanisms and processes in the reactor—is, of course, dubious. Therefore, despite being the most examined model of macromixing, the SDM is also the most discussed model, and many problems concerning both its nature and application remain unresolved.

Justification of the standard dispersion model

A wide application of the dispersion model began forty years ago when numerous authors noticed that longitudinal mixing can be treated the same as diffusion; see Levenspiel and Smith (1957). The most notable is the work of Danckwerts (1953) and Taylor (1953, 1954a,b) who in pioneering papers introduced the concept of longitudinal dispersion superimposed on plug flow to describe the fact that not all fluid elements travel at equal speed through a system.

The Fickian type of dispersion equation, Eq. 1, with boundary conditions, Eq. 2, was proposed by Danckwerts for a rough description of longitudinal mixing on the basis of a likeness between longitudinal mixing and random walk.

Taylor (1953, 1954a) investigated the way in which a liquid spreads out longitudinally as it moves down a straight tube and demonstrated by a few careful experiments and a novel mathematical analysis of a rather heuristic kind, that far downstream of the source the longitudinal spread is equivalent to a diffusion process; he also provided estimates for the longitudinal dispersion coefficient. Since then the notion of a longitudinal dispersion has been recognized as being relevant in a wide variety of contexts, like in flows in rivers and estuaries, in oil pipelines, in water mains, in pneumatic and hydraulic industrial devices, in blood vessels, in tubules in plants. An enormous variety of extensions and generalizations of Taylor's simple result for steady flow in a straight circular tube has been developed; see Batchelor (1981). The most notable developments of the classical asymptotic theory of Taylor, while still preserving the basic ideas of his original work, were produced by Aris (1956), Horn (1971), and Brenner (1980, 1982). Considerable attention has also been paid to the one-dimensional dispersion of solute during relatively short times, too short for the macrotransport process to be fully established; see Philip (1963), Gill (1967), Gill and Sankarasubramanian (1970, 1972), DeGance and Johns (1978a,b, 1980), Hatton and Lightfoot (1982, 1984a,b), Yamanaka (1983a,b), Yamanaka and Inui (1994), and Smith (1981, 1987). The importance for practice of the diffusion analysis of Taylor and the subsequent investigations lies in the ability of the one-dimensional transport equation to take into account complicated velocity and concentration profiles in a simple manner, as well as providing a theoretical framework for the dispersion coefficient D_e.

The proposed generalizations of Taylor's dispersion theory essentially extend its possibilities, but are not an additional substantiation of the SDM of Eqs. 1 and 2. The elegant mathematical properties of diffusion-type equations should not obscure the fact that their application in a certain situation requires a physical justification. The resemblance of longitudinal mixing and random walk or ordinary molecular diffusion is only a weak justification to describe chemically reactive systems with Eqs. 1 and 2 and specified boundary conditions. The application of Fick's law for the description of longitudinal dispersion is questionable since time and velocity scales of the longitudinal dispersion process are essentially different from those for ordinary molecular diffusion (see Fischer et al., 1979); they are comparable to the characteristic times and velocities in a reactor system, like reaction time and residence time.

We should be well aware that Taylor (1954b) clearly determined the region of applicability of his results and that Danckwerts (1953) formulated the limitations of his model. At the end of his article, Danckwerts states, "the foregoing treatment of reactors will seldom be applicable to practical problems except as a rough guide."

Shortcomings of the standard dispersion model

Numerous investigations show the popular SDM should be used with some circumspection for analysis of chemical reactors and contactors. It often fails because the dispersion coefficient as computed from exactly calculated concentration profiles depends not only on the flow conditions, the geometry, and physical properties as customarily assumed, but also on time, longitudinal position, initial and boundary conditions, and chemical reaction rates; see Whitaker (1971), Carbonell and McCoy (1978), Nigam and Vasudeva (1976, 1977). The dispersion coefficient even becomes negative in some situations, for example, for short distances from the inlet; see Carbonell and McCoy (1978). Such effects become especially pronounced for multiphase reactive systems and when surface reaction and adsorption take place. This has been demonstrated by many investigators, such as Sankarasubramanian and Gill (1973, 1974), Hatton and Lightfoot (1982, 1984a,b), and Paine et al. (1983). So the approximate flow model of Eqs. 1 and 2 may provide a fair description in one situation, but may be completely inadequate in another, even in the same type of vessel. These aspects cast considerable doubt on the significance of the dispersion coefficient as an independent design variable and on the utility of the SDM as a whole.

When the dispersion coefficient D_e is no longer only determined by the hydrodynamical and physical properties of the system, its determination generally becomes a problem that is as difficult to solve as the complete multidimensional problem; this deprives the model of the fundamental advantage of its simplicity! In some cases the dispersion coefficient can be obtained only empirically after finding the correct solution of the problem; see Nigam and Vasudeva (1976, 1977) and Kulkarni and Vasudeva (1976). In such cases, of course, the SDM is of little value since it is not more than an empirical correlation: no physical meaning can be attached to an equation in which the dispersion coefficient is not a system property but a function determined by the problem at hand.

The SDM is substantially deficient in details. It is difficult to reconcile Eq. 1 with the underlying physical processes (see Sundaresan et al., 1980). The mathematical structure of model equation Eq. 1 being a second-order, parabolic-type differential equation involves the instantaneous influence of a concentration change in all points in the system, both upstream and downstream, and with an intensity determined by the effective dispersion coefficient. This is acceptable only when molecular diffusion is the main cause of the longitudinal mixing. It is assumed, of course, that the flow velocity is much lower than the velocity of sound. For most real systems of practical interest longitudinal dispersion is essentially a mixing process, whereby the entire longitudinal transfer of mass is due to convection, and whereby changes of concentration at some point spread out in the longitudinal direction with forward and backward velocities that do not exceed the maximum velocities of the convective motion in these directions.

For a longitudinal dispersion problem the relation between the apparent longitudinal dispersion and backmixing is significant. Correct accounting for feedback in a model is essential for the formulation of reasonable boundary conditions and for the analysis of dynamic phenomena, where the course of a process depends on the intensity of feedback, that is, of fluid flow against the direction of the main stream. The situation in a local region in a reactor depends greatly on the presence or absence of such backflows; see Wilhelm (1962). The fundamental difference between longitudinal dispersion and backmixing has been demonstrated by Westerterp and Landsman (1962) and Westerterp and Meyberg (1962) for the flow in a rotating disk contactor. This difference cannot be described by a Fickian dispersion model, in which backflow against the main stream with an intensity equal to the apparent dispersion is an inherent part of that model. In a wide class of real systems with an apparent longitudinal dispersion actually very little back diffusion occurs. This absence of back transport was demonstrated experimentally by Westerterp and Meyberg (1962) in a rotating disk contactor with liquid flow alone and under conditions of no rotation; by Hiby (1962) at moderate and high Reynolds numbers in packed beds; and by Deckwer and Maehlmann (1974, 1976) in liquid flowing through a reactor divided into three sections of different properties.

It should be observed that the violation of reality by the SDM, for example, of a longitudinal feedback, leads to the necessity of formulating boundary conditions for Eq. 1, which by no means relate to what really happens at the boundaries of the system. This discrepancy between the SDM and real systems is the reason for the ever continuing discussion of Danckwerts' boundary conditions, Eq. 2, and the various modifications proposed since Danckwerts (1953). His boundary conditions or more general ones can be obtained correctly in case longitudinal mixing is realistically described by Fick's law, thus determined by molecular diffusion; see Wehner and Wilhelm (1956), Pearson (1959), Bischoff (1961), Van Cauwenberghe (1966), and Choi and Perlmutter (1976). The boundary conditions, Eq. 2, have been correctly criticized in the realistic physical situation, where molecular diffusion in longitudinal direction can be neglected; see Wissler (1969), Wicke (1975), Deckwer and Maehlmann (1976), and Carbonell and McCoy (1978). A direct experimental proof of the boundary conditions never has been published.

In spite of the numerous experimental and theoretical investigations of longitudinal dispersion that have been published, surprisingly little attention has been paid to uncovering the underlying phenomena through a detailed analysis of longitudinal mixing. One of the most notable investigations undertaken to give a rational explanation or a reexamination of the problem was made by Sundaresan et al. (1980), who made a detailed examination of dispersion in a fixed bed, taking into account the fine structure of the model and the necessity of specifying not only initial but also boundary conditions. The only questionable point in the work is the combination of the mathematical properties of second-order hyperbolic equations with physics inherent to pure diffusion processes. As a consequence, after a detailed examination of dispersion in a fixed bed, these authors concluded that no linear continuous partial differential equation of finite order can ever satisfy the physical requirements and that no single model has outstanding advantages over any other. Otherwise, Stewart (1965) suggested wave equations instead of diffusional-type relations for fixed-bed reactors. Later work of Thacker (1976), Maron (1978), Smith (1981), Dil'man and Kronberg (1983), and Van den Broeck (1990) shows that hyperbolic equations can be used for an accurate description of the distribution of a contaminant, not only for an asymptotically long time but also for short and intermediate time periods after an initial concentration disturbance has been introduced into the flow.

Our approach

For the reasons mentioned earlier we may state with Sundaresan et al. (1980): "... one is left with the uneasy feeling that there is need for rational explanation or reexamination of the problem." Therefore we again studied the problem of the description of a dispersed flow system, attempting to take into account the physical features of the problem.

The main ideas justifying the Fickian-type dispersion model were formulated by Danckwerts (1953) and Taylor (1953, 1954a,b). Therefore we will reconsider their ideas to obtain a simple alternative to the Fickian-type dispersion model. We will demonstrate that only minor changes to Taylor's and Danckwerts' ideas are sufficient to obtain a model absolutely different from and equally as simple as the SDM. The motivation of our approach is treated here; the potential benefits and applications will follow in sequels to this article.

In the first part a multidimensional convective-diffusion equation, containing the main features of a wide class of problems, is considered; a nonlinear source term explicitly independent of transverse coordinates is also included. The object of this part is to reexamine Taylor's well-thought-out problem from a different point of view. It will be shown that accounting for significant features of longitudinal mixing gives rise to a quasi-linear hyperbolic system of two first-order equations for the average concentration and the dispersion flux, in case molecular diffusion in the longitudinal direction can be neglected. The model equations are obtained from a multidimensional convective diffusion equation on the basis of minor extensions to the heuristic equilibrium analysis of Taylor. For a better understanding of the derivation of the model equations the classic case of laminar flow in a circular tube is studied. The mathematical treatment of the more general problem is set forth in the Appendix.

In the second part of the article the hyperbolic transport equations are derived in a simple way at a particle level of scrutiny, being these particles' molecules, Brownian particles, or elements of fluid representing solute mass in the sense of Danckwerts (1953). The derivation is based on accounting for the finite velocity of the particles and gives a physical interpretation of the equations obtained in the first part. Since this qualitative approach is more general, it must lead to a better understanding of the mechanisms responsible for the characteristics of the longitudinal dispersion phenomena and it must also help us understand the limitations of the equations obtained in the first part.

The new model introduced in this article also may be called a dispersed plug-flow model. To distinguish it from the traditional model we will call it the "wave model" in contrast to the Fickian-type or standard dispersion model.

It is shown that, contrary to the cited conclusion of Sundaresan et al. (1980), for linear problems, the average concentration and the dispersion flux obey a hyperbolic equation of the second order, which satisfies the no-backmixing requirement for unidirectional flow. The proposed wave model contains three parameters that depend only on the flow conditions, physical properties, and geometry. It effectively resolves the problem of boundary conditions. For unidirectional flow these are formulated only at the reactor inlet. An important peculiarity of the new equation for the dispersion flux, proposed instead of Ficks' law, is the presence of derivatives of the dispersion flux toward time and the longitudinal coordinate as well as a derivative of the source term q with respect to concentration. The causes of the shortcomings of the SDM will be made evident.

Development of a New Longitudinal Dispersion Model following Taylor's Approach

For a better understanding of the derivation of a new longitudinal dispersion model we first elaborate on the case of *dispersion of a solute in a laminar flow* through a tube as considered by Taylor in his classic 1953 article. The concentration of the solute is described by the convective diffusion equation

$$\frac{\partial c}{\partial t}+u\frac{\partial c}{\partial x}=D\left(\frac{\partial^2 c}{\partial r^2}+\frac{1}{r}\frac{\partial c}{\partial r}\right) \qquad (3)$$

along with the following boundary conditions

$$\frac{\partial c}{\partial r}=0 \quad \text{at} \quad r=0,\, a \qquad (4)$$

where a is the tube radius and the velocity u is given by

$$u=2\bar{u}\left(1-\frac{r^2}{a^2}\right).$$

Throughout this article an overbar on a quality denotes its cross-sectionally averaged value, as defined for an axisymmetrical problem in a tube by

$$\overline{(\ldots)}=\frac{2}{a^2}\int_0^a(\ldots)r\,dr.$$

We have neglected the molecular diffusion in axial direction, as Taylor (1953) did, on the assumption that the longitudinal mixing is completely dominated by shear dispersion. This assumption is used here deliberately in order to separate the different mechanisms of longitudinal mixing; it makes the problem easier to understand at the initial stage of our approach.

Here again our problem is one of suitably describing the longitudinal dispersion characteristics of a system in terms of a one-dimensional dispersed plug-flow model, in which longitudinal dispersion is caused by the combined effect of convection and transverse diffusion.

Our first step in the development of our axial dispersion model is to take the area average of Eq. 3. We obtain:

$$\frac{\partial \bar{c}}{\partial t}+\bar{u}\frac{\partial \bar{c}}{\partial x}+\frac{\partial j}{\partial x}=0 \qquad (5)$$

where

$$j=\frac{2}{a^2}\int_0^a\bar{u}\left(1-2\frac{r^2}{a^2}\right)cr\,dr \qquad (6)$$

is the mass flux density across a plane that is perpendicular to the x-axis and that moves with the mean flow speed. This flux density is sometimes called the diffusive or diffusional flux. We will call it the dispersion flux to stress its difference from the diffusive flux due to molecular diffusion. The value of the dispersion flux is determined by interaction between the transverse diffusion and the velocity profile; see also Aris (1967).

In order to obtain closure of Eq. 5, a constitutive equation is needed for the dispersion flux, which cannot be related directly to $\bar{c}$. This problem is common to all convective dispersion studies, and the procedures as developed by Gill and Sankarasubramanian (1970), Johns and DeGance (1975), DeGance and Johns (1978a,b), and Smith (1981, 1987) are all attempts to circumvent this difficulty. Here, we apply another approach based on the method outlined by Taylor (1953).

When the transverse variations of the concentration are small—the system is close to equilibrium—we can find a first approximation for the concentration $c^{(1)}$ from Eq. 3, in which some averaged concentration $\overline{c^{(0)}}$ is used in the lefthand side instead of c:

$$\frac{\partial \overline{c^{(0)}}}{\partial t}+u\frac{\partial \overline{c^{(0)}}}{\partial x}=D\left(\frac{\partial^2 c^{(1)}}{\partial r^2}+\frac{1}{r}\frac{\partial c^{(1)}}{\partial r}\right). \qquad (7)$$

Taking the area average of Eq. 7, we find the solvability condition for this equation

$$\frac{\partial \overline{c^{(0)}}}{\partial t} + \bar{u}\frac{\partial \overline{c^{(0)}}}{\partial x} = 0, \tag{8}$$

which corresponds to the plug flow model. Subtracting Eq. 8 from Eq. 7, we obtain

$$(u - \bar{u})\frac{\partial \overline{c^{(0)}}}{\partial x} = D\left(\frac{\partial^2 c^{(1)}}{\partial r^2} + \frac{1}{r}\frac{\partial c^{(1)}}{\partial r}\right). \tag{9}$$

The solution of Eq. 9 with the boundary conditions Eq. 4 is

$$c^{(1)} = \overline{c^{(1)}} + g_1 \frac{\partial \overline{c^{(0)}}}{\partial x} \tag{10}$$

where

$$g_1 = -\frac{\bar{u}a^2}{4D}\left(\frac{1}{3} - \rho^2 + \frac{1}{2}\rho^4\right), \quad \rho = \frac{r}{a},$$

as was already proved by Taylor (1953).

If we substitute Eq. 10 into Eq. 6, we find the well-known equation for the dispersion flux:

$$j^{(1)} = -D_e \frac{\partial \overline{c^{(0)}}}{\partial x}; \qquad D_e = \frac{a^2 \bar{u}^2}{48D}. \tag{11}$$

Equations 5 and 11 are equivalent to Taylor's result, if we additionally suppose that $j^{(1)}$ and $\partial \overline{c^{(0)}}/\partial x$ cannot be distinguished from j and $\partial \bar{c}/\partial x$. It shows, in particular, that the same phenomenon may be described by equations of a different complexity and with different qualitative properties: according to Eq. 3 for a laminar flow system the whole longitudinal transfer of matter occurs solely as a result of convective motion with a velocity that does not exceed the maximum flow velocity, whereas Eqs. 5 and 11 predict an infinite velocity of signal propagation. The importance of this result of Taylor is well known: the rather complicated multidimensional Eq. 3 can be represented by the much simpler Eq. 1 with $q = 0$. However, Eq. 11 is applicable only for slow spatial variations in and slow temporal evolutions of the concentration. For setting up the boundary conditions and for resolving other problems, where a finite speed of signal propagation or the intensity of the real backmixing are important, this qualitative difference of the starting Eq. 3 and Eqs. 5 and 11 becomes unacceptable. Therefore, we will try to find a simple one-dimensional equation without the aforementioned shortcomings, maintaining the main qualitative features of the original multidimensional Eq. 3. It should be noted that the use of Eq. 10 to find the dispersion flux is not logical in the context of the applied closure procedure, because the mass conservation equation, Eq. 8, at this stage does not yet contain the dispersion flux.

In obtaining a constitutive equation for the dispersion flux we shall consider Eqs. 10 and 11 only as an intermediate step: from these equations it follows that the concentration can be represented in the form:

$$c^{(1)} = \overline{c^{(1)}} - \frac{g_1}{D_e} j^{(1)}. \tag{12}$$

We will use Eq. 12 assuming the dispersion flux $j^{(1)}$ to be an unknown variable in this equation. In this way, Eq. 12 is a more general relationship than Eq. 10, because $j^{(1)}$ does not necessarily obey Eq. 11. Equation 10 is true only when the concentration distribution is close to equilibrium and it is clearly incorrect in certain other applications: it fails specifically when the concentration itself depends on x and the average concentration does not. From a quantitative point of view Eq. 12 may not be entirely correct for concentration distributions far from equilibrium, but qualitatively it is correct in all cases where the concentration can be approximated by $c = \bar{c} + \phi(r)\psi(x, t)$, with arbitrary functions ϕ and ψ. In our approach the local concentration is expressed in terms of the average area concentration and the dispersion flux. This use of the dispersion flux in an explicit form in the expression for c represents a key departure from the well-known Gill-Subramanian (1970) expansion for c and other expansions for c used to obtain a closure of Eq. 5. In previous work an expression for c has been sought first of all in terms of a suitably defined average concentration and its axial derivatives and not so for the flux j; see Gill (1967), Chatwin (1970), Carbonell (1980), Paine et al. (1983), Hatton and Lightfoot (1982, 1984a).

Replacement of Eq. 11 by Eq. 12 does not resolve the closure problem. At this point we will repeat Taylor's procedure using Eq. 12 instead of the area averaged concentration $\overline{c^{(0)}}$. It is important that Eq. 12 not contain derivatives, which therefore enables us to apply the procedure a second time without increasing the order of the constitutive equation.

On substituting Eq. 12 into the lefthand side of Eq. 3, we have an equation for a more precise concentration distribution $c^{(2)}$:

$$\frac{\partial \overline{c^{(1)}}}{\partial t} + u\frac{\partial \overline{c^{(1)}}}{\partial x} - \frac{g_1}{D_e}\left(\frac{\partial j^{(1)}}{\partial t} + u\frac{\partial j^{(1)}}{\partial x}\right) = D\left(\frac{\partial^2 c^{(2)}}{\partial r^2} + \frac{1}{r}\frac{\partial c^{(2)}}{\partial r}\right). \tag{13}$$

Averaging Eq. 13 over the cross section, we obtain the condition for its solvability:

$$\frac{\partial \overline{c^{(1)}}}{\partial t} + \bar{u}\frac{\partial \overline{c^{(1)}}}{\partial x} + \frac{\partial j^{(1)}}{\partial x} = 0, \tag{14}$$

which is the mass conservation equation. Taking Eq. 14 into account and boundary conditions Eq. 4, the solution of Eq. 13 is

$$c^{(2)} = \overline{c^{(2)}} + g_1\frac{\partial \overline{c^{(1)}}}{\partial x} - g_2\frac{\partial j^{(1)}}{\partial t} - (g_2\bar{u} + g_3)\frac{\partial j^{(1)}}{\partial x} \tag{15}$$

where

$$g_2 = \frac{a^2}{4\bar{u}D}\left(\frac{7}{6} - 4\rho^2 + 3\rho^4 - \frac{2}{3}\rho^6\right);$$

$$g_3 = \frac{a^2}{4D}\left(\frac{31}{60} - 3\rho^2 + 5\rho^4 - \frac{10}{3}\rho^6 + \frac{3}{4}\rho^8\right).$$

Substituting Eq. 15 into Eq. 6 we find the new constitutive equation for the dispersion flux:

$$j^{(2)} + \frac{1}{15}\frac{a^2}{D}\left(\frac{\partial j^{(1)}}{\partial t} + \frac{5}{4}\bar{u}\frac{\partial j^{(1)}}{\partial x}\right) = -D_e\frac{\partial \overline{c^{(1)}}}{\partial x}. \tag{16}$$

If we assume that $\overline{c^{(1)}} \approx \bar{c}$ and $j^{(1)} \approx j^{(2)} \approx j$, we obtain from Eqs. 14 and 16 one-dimensional equations that are more general than the plug-flow model:

$$\frac{\partial \bar{c}}{\partial t} + \bar{u}\frac{\partial \bar{c}}{\partial x} + \frac{\partial j}{\partial x} = 0 \tag{17}$$

$$j + \frac{1}{15}\frac{a^2}{D}\left(\frac{\partial j}{\partial t} + \frac{5}{4}\bar{u}\frac{\partial j}{\partial x}\right) = -D_e\frac{\partial \bar{c}}{\partial x}. \tag{18}$$

The second equation essentially differs from the equation obtained by Taylor (1953) because of the two derivatives in the lefthand side.

The procedure used for deriving Eqs. 17 and 18 from Eqs. 3 and 4 can be applied with some minor changes for a *three-dimensional convective diffusion equation* that is more general than Eq. 3:

$$\frac{\partial c}{\partial t} + u(y, z)\frac{\partial c}{\partial x} + q(c, x, t) = \nabla(D_t\nabla c) \tag{19}$$

with

$$D_t\mathbf{n}\nabla c = 0 \qquad \text{on} \qquad \partial A. \tag{20}$$

Here the longitudinal velocity u and the transversal dispersion coefficient D_t are arbitrary functions of the transversal coordinates y and z, and ∇ is the two-dimensional gradient operator $(\partial/\partial y, \partial/\partial z)$. The component consumption rate q in Eq. 19 is assumed to depend on concentration, time, and the axial coordinate. As before in the case of laminar flow through a tube, we have ignored a local longitudinal diffusion or dispersion. For simplicity we also do not consider an evident dependence of the component consumption term on the transverse coordinates.

Applying the procedure used for the derivation of Eqs. 17 and 18 from Eqs. 3 and 4—with some nonessential changes—to Eqs. 19 and 20 gives rise to a system of two one-dimensional equations more general than Eqs. 17 and 18, see also the Appendix:

$$\frac{\partial \bar{c}}{\partial t} + \bar{u}\frac{\partial \bar{c}}{\partial x} + \frac{\partial j}{\partial x} + q(\bar{c}, x, t) = 0 \tag{21}$$

$$(1 + \tau q'(\bar{c}, x, t))j + \tau\frac{\partial j}{\partial t} + \tau(\bar{u} + u_a)\frac{\partial j}{\partial x} = -D_e\frac{\partial \bar{c}}{\partial x}. \tag{22}$$

Here $j = \overline{(u - \bar{u})c}$ and the prime indicates the derivative with respect to c, so $q' = \partial q/\partial c$. The cross-sectionally averaged values are defined by

$$\overline{(\ldots)} = \frac{1}{A}\int(\ldots)\,dA.$$

The parameters of the Eq. 22 are

$$D_e = -\overline{(u - \bar{u})g_1}; \qquad \tau = \frac{\overline{g_1^2}}{D_e}; \qquad u_a = \frac{\overline{(u - \bar{u})g_1^2}}{D_e\tau} \tag{23}$$

where function g_1 satisfies the equation

$$\nabla(D_t\nabla g_1) = u - \bar{u} \tag{24}$$

with

$$\overline{g_1} = 0 \qquad \text{and} \qquad D_t\mathbf{n}\nabla g_1 = 0 \qquad \text{on} \qquad \partial A. \tag{25}$$

Equation 21 is the standard mass conservation equation, whereas Eq. 22 is new. In comparison to Fick's law in the SDM it contains the derivatives of the dispersion flux with respect to time and the longitudinal coordinate, as well as the derivative of the source term with respect to the concentration. The new model of Eqs. 21 and 22 contains three parameters D_e, τ, and u_a, which can be calculated from Eqs. 23, 24, and 25, provided the velocity profile and the transverse dispersion coefficient are known. For instance, for laminar flow in a tube $D_e = a^2\bar{u}^2/(48D)$, $\tau = a^2/(15D)$, and $u_a = \bar{u}/4$. Their experimental determination and their influence on dispersion will be discussed later.

For flows where the gradient operator ∇ is one-dimensional, Eq. 24 is an ordinary differential equation and can be integrated explicitly. For example, for axially symmetrical situations in a tubular reactor holds:

$$g_1(r) = \int_0^r\left(\frac{1}{r'D_t}\int_0^{r'} r''(u - \bar{u})dr''\right)dr' + k_1$$

where k_1 is the integration constant, defined by the condition $\bar{g}_1 = 0$. In this case D_e in Eq. 23 is the same longitudinal dispersion coefficient as found by Bischoff and Levenspiel (1962) for the SDM. The general solution of Eq. 24 is presented in the Appendix, where it is also shown that $D_e > 0$ and, according to Eq. 23, $\tau > 0$ hold for arbitrary nonuniform flow. The quasi-linear, first-order system of Eqs. 21 and 22 is hyperbolic with the following characteristic velocities (see Whitham, 1974):

$$u_{1,2} = \bar{u} + \frac{u_a}{2} \pm \sqrt{\frac{u_a^2}{4} + \frac{D_e}{\tau}}\,.$$

The velocity of one wave is larger and the other one is smaller than the average velocity $\bar{u}$. Using Eqs. 23 we find for unidirectional flow or $u \geq 0$:

$$\bar{u} + \frac{u_a}{2} = \frac{\bar{u}\overline{g_1^2} + \overline{ug_1^2}}{2\overline{g_1^2}} > 0$$

$$\left(\bar{u} + \frac{u_a}{2}\right)^2 - \left(\frac{u_a^2}{4} + \frac{D_e}{\tau}\right) = \frac{\bar{u}\overline{ug_1^2} - (\overline{ug_1})^2}{\overline{g_1^2}} > 0$$

where the last inequality is a consequence of the Schwartz inequality. The preceding inequalities mean that $u_{1,2} > 0$, so that both waves only move downstream. This requires that the two boundary conditions for Eqs. 21 and 22 be specified only at the inlet. The appropriate initial and boundary conditions at the reactor entrance for Eqs. 21 and 22 are apparent. They immediately follow from the initial and boundary conditions for the original Eq. 19. If for Eq. 19 the concentration is specified at $x = 0$ and at $t = 0$,

$$x = 0, \qquad c = \zeta_0(y, z, t); \qquad t = 0, \qquad c = \zeta_{\text{in}}(x, y, z),$$

then the initial and boundary conditions for Eqs. 21 and 22 are

$$t = 0, \qquad \bar{c} = c_{\text{in}}(x) = \overline{\zeta_{\text{in}}}, \qquad j = j_{\text{in}}(x) = \overline{(u - \bar{u})\zeta_{\text{in}}} \quad (26)$$

$$x = 0, \qquad \bar{c} = c_0(t) = \overline{\zeta_0}, \qquad j = j_0(t) = \overline{(u - \bar{u})\zeta_0} \quad (27)$$

where the subscript "in" has been used for the initial moment $t = 0$ and the subscript "0" for the location $x = 0$.

For special cases of the source term q, Eqs. 21 and 22 may be transformed to one second-order hyperbolic equation. In particular, for a first-order chemical reaction with a position- and time-independent rate constant k, or where $q = kc$, we find after elimination of the dispersion flux from Eqs. 21 and 22, the equation for the average concentration only:

$$\frac{\partial^2 \bar{c}}{\partial t^2} + (2\bar{u} + u_a)\frac{\partial^2 \bar{c}}{\partial x \partial t} + (\bar{u}^2 + \bar{u}u_a - D_e/\tau)\frac{\partial^2 \bar{c}}{\partial x^2} + (\tau^{-1} + 2k)\frac{\partial \bar{c}}{\partial t} + (\bar{u}/\tau + k(2\bar{u} + u_a))\frac{\partial \bar{c}}{\partial x} + k(\tau^{-1} + k)\bar{c} = 0. \quad (28)$$

The equation for the dispersion flux has a similar appearance, since Eqs. 21 and 22 are linear and have constant coefficients. Equation 28 for the case of a source term independent of the concentration was also obtained by Smith (1981) for his particular problem, on the basis of quite a different, also heuristic, mathematical analysis.

The initial and boundary conditions for Eq. 28, resulting from Eqs. 21 and 22 and their initial and boundary conditions Eqs. 26 and 27, are

$$t = 0, \qquad \bar{c} = c_{\text{in}}(x), \qquad \frac{\partial \bar{c}}{\partial t} = -\left(\bar{u}\frac{\partial c_{\text{in}}}{\partial x} + \frac{\partial j_{\text{in}}}{\partial x} + kc_{\text{in}}\right) \quad (29)$$

$$x = 0, \qquad \bar{c} = c_0(t),$$

$$\frac{\partial \bar{c}}{\partial x} = -\frac{(\bar{u} + u_a)\left(\frac{\partial c_0}{\partial t} + kc_0\right) - \frac{\partial j_0}{\partial t} - (\tau^{-1} + k)j_0}{\bar{u}(\bar{u} + u_a) - D_e/\tau}. \quad (30)$$

For a uniform distribution of the concentration over the cross section at the initial moment and at the inlet $j_{\text{in}} = j_0 = 0$.

The procedure used to obtain Eqs. 21 and 22 can be continued to the next levels, resulting in new one-dimensional equations and new unknown functions of the longitudinal coordinate and of time, in addition to the average concentration and dispersion flux. More exact one-dimensional equations will include more parameters, whose values in the general case have to be determined by experiment.

A Qualitative Development of the New Model, following the Danckwerts Approach

A qualitative explanation of longitudinal dispersion phenomena was given forty years ago by numerous authors who recognized that longitudinal dispersion is similar to a diffusion process. The main ideas were formulated by Danckwerts (1953) for flow through a bed of solids. According to him each element of the fluid travels at the same average velocity and experiences fluctuations of the same average magnitude and frequency. Therefore, the ordinary "random walk" theory can be applied to such behavior and as a result the longitudinal mixing is described by the diffusion law (Danckwerts, 1953). This reasoning is also applicable to arbitrary, nonuniform flow with transverse mixing; it qualitatively corresponds to Taylor's (1953, 1954a) results, see also Fischer et al. (1979). The problem is to find the equation for the diffusion or dispersion flux. Usually, as Danckwerts supposed, the diffusion law is identified by Fick's law:

$$j = -D\frac{\partial c}{\partial x}. \quad (31)$$

The resemblance between longitudinal dispersion and molecular diffusion is evident. This resemblance, however, is not a proof for the Fickian nature of longitudinal dispersion because the time, distance, and velocity scales of these two phenomena are absolutely different (see Fischer et al., 1979).

For Fick's law certain conditions are assumed to hold. In particular, on the particle level of scrutiny it is supposed that both the mean particle free path λ and the mean time of free flight τ approach zero in such a way that the ratio $\lambda^2/(2\tau) = D$ remains finite. As is well known a key requirement for this limit to be reasonable from a physical point of view is that the instantaneous particle velocity $v = \lambda/\tau$ must be much larger than other characteristic velocities, for example, the average convective velocity $\bar{u}$. Application of Fick's law, when this condition is not fulfilled, leads to erroneous results. In particular the propagation speed of concentration disturbances in accordance to Fick's law is infinitely fast. As a rule, the just cited conditions are reasonable when applied to ordinary molecular diffusion. For example, for molecular diffusion in gases under normal conditions the mean free path time of the molecules is of the order of 10^{-9}–10^{-11} s, and the mean velocity of a molecule of the order of 10^2–10^3 m/s.

These scales are incomparable to other characteristic times and velocities in chemical reaction engineering processes. Therefore without serious mistakes we may assume the mean free time equals zero, and the mean velocity equals infinity. Only the product of these values, determining the diffusion coefficient, is finite and does not equal zero. For the longitudinal dispersion phenomenon the fluid elements are dispersed in the axial direction according to a random process with quite different length and time scales. The time scale of the elements is equal to the "time of decay" introduced by Taylor (1953) in the case of shear dispersion, and the mean velocity is of the order of the mean flow velocity. Consequently, the time and velocity scales for longitudinal dispersion are comparable to the other time and velocity scales of the reactor process. Therefore, we generally have no grounds to neglect their values, as for molecular diffusion, assuming a velocity equal to infinity and the mean free path time equal to zero. This is the main shortcoming of the standard dispersion model. And we need to discuss Fick's law critically.

The simplest explanation of Fick's law is provided by the elementary concepts of the classic kinetic theory. We therefore will follow the reasoning of Feynman et al. (1966) to illustrate the mechanisms involved, to prove on the one hand a qualitative ground for Eq. 22, and on the other hand to explain the physical nature of wave equations for dispersion phenomena.

Following Feynman, suppose we have a container of gas in thermal equilibrium and introduce a small amount of a different kind of gas at some place in the container that we shall call the "special" gas. We now compute the net flow of the molecules of the special gas in the x-direction and consider an imaginary plane surface of one unit area perpendicular to the x-axis. To count the number of special molecules crossing this plane in a time Δt, we take the number of molecules in a volume extending the distance $v\Delta t$ from the plane. Here v is the average actual molecular velocity. The numbers of special molecules that pass from left to right and from right to left are $n_{-}v\Delta t$ and $n_{+}v\Delta t$, where n_{-} and n_{+} are the numbers of special molecules per unit volume on the left- and righthand sides of the plane, respectively. The molecular current is

$$j = \frac{n_{-}v\Delta t - n_{+}v\Delta t}{\Delta t} = (n_{-} - n_{+})v.$$

By n_{-} we mean the density at a distance to the left equal to the mean free path λ, and by n_{+} the density at the distance λ to the right of our imaginary surface. In terms of a continuous function of $c(x)$ describing the distribution of special molecules in space, we can express the diffusion flux in the form of Fick's law, Eq. 31, where D is a coefficient proportional to $v\lambda$. To find this diffusion flux several rough approximations have been made (see Feynman et al., 1966).

This brief traditional explanation of Fick's law does not take into consideration a fundamental feature of the problem: the molecules do not cover their free path λ instantaneously. The moments of time in the left and right sides of Eq. 31 differ in time by approximately the mean time between collisions of $\tau = \lambda/v$. Consequently, the diffusion flux at the moment t is determined by the concentration gradient at the preceding moment $t-\tau$ and, more correctly than Fick's approach, should be

$$j(t+\tau) = -D\frac{\partial c(t)}{\partial x}. \tag{32}$$

Expanding the lefthand side of Eq. 32 for small values of τ in a Taylor series, we obtain, neglecting terms of a higher order,

$$j + \tau\frac{\partial j}{\partial t} = -D\frac{\partial c}{\partial x}. \tag{33}$$

This equation, combined with the mass conservation equation, leads to a second-order hyperbolic equation for the concentration or the diffusion flux. Equation 33 is not new. Actually, it has been rediscovered over and over again. Application of Eq. 33 instead of Eq. 31 avoids the infinite velocity of signal propagation. In the theory of transport phenomena an equation of the form of Eq. 33 was first proposed by Maxwell (1867) for the description of the relation between stress and strain in a viscous body; now it is well known as Maxwell's model for a viscoelastic fluid; see Joseph (1990). In the diffusion theory, Eq. 33 was first derived by Fock (1926). Afterwards, Eq. 33 was derived again in different ways and for different purposes (see Davidov (1935), Goldstein (1951), and Davies (1954)). Analogous generalizations are known for Fourier's law of heat conduction; see Cattaneo (1948) and Vernotte (1958); for turbulent diffusion, see Luikov (1966); and for momentum fluxes in turbulent flows, see Builtjes (1977). Note that for molecular diffusion, the time, τ, as a rule is very small in comparison to characteristic times and Eqs. 31 and 33 are distinguishable only qualitatively.

It is worth mentioning that Eq. 33 cannot be taken to be generally applicable, since in particular the partial derivative with respect to time is not frame-invariant. In Eq. 33 j is defined in a system without net volume flux.

The preceding derivation of an equation for the diffusion or dispersion flux is illustrative only, but it shows in a simple way the physical background of hyperbolic transport equations. The derivation of Eq. 33 is true only for slowly varying concentration fields when a one-term Taylor expansion is permissible. From our derivation in particular, it is not clear what equation must be used instead of Eq. 33 when the concentration noticeably changes during a time period of the free path, τ, or on the length of the mean free path, λ. To this end a more general approach to the diffusion or dispersion process is given below. For reasons of simplicity we restrict our discussion to the one-dimensional case, which is the one of major interest in applications to longitudinal dispersion phenomena.

Consider continuous random walks of particles—in a coordinate system with no convective flow of the particles—along a straight line with two constant velocities v_{+} in the positive direction of the x-axis and v_{-} in the negative direction, respectively. By particle we mean a molecule of a special gas or, as in Fischer et al. (1979), any sufficiently small but identifiable, neutrally buoyant entity whose size is such that its dynamical behavior is essentially indistinguishable from that of the fluid. We assume each particle undergoes instantaneous interactions with its surroundings, as a consequence of which the particle starts a new partial path; there is a probability, p_+, that it will move with a velocity v_+ and a probability of $p_- = 1 - p_+$ that the velocity will be v_-. The time spent moving in a certain direction after a collision and before the following collision is assumed to be a random variable characterized by a probability depending only on this period. To find the net flow we again count the number of particles crossing at time t the unit surface area located at point x. We characterize the particles crossing that plane at moment t by the location of their last collision. The particles, reaching the point x at the moment t from left to right, had their last collision at the time $t - \eta$ and at the point $x - \eta v_+$ ($\eta > 0$), obtained a velocity v_+ in the direction of the plane, moved during time η without collisions, and did not disappear due to a chemical reaction. The total number of collisions at point $x - \eta v_+$ and at time $t - \eta$ in terms of the continuous function $c(x, t)$, describing the distribution of the particles along the x-axis, is equal to $c(x - \eta v_+, t - \eta)/\tau$, where τ is the mean period of time between collisions. So the flux of particles at point x and at time t from left to right can be written as

$$j_+(x, t) = \frac{p_+ v_+}{\tau} \int_0^\infty G(\eta) H(\eta) c(x - \eta v_+, t - \eta)\, d\eta \quad (34)$$

where $G(\eta)$ and $H(\eta)$ are the probabilities that a particular particle survives a time η without collisions and does not disappear due to a chemical reaction during this time, respectively. The flux of particles at point x and at time t from right to left is, similarly:

$$j_-(x, t) = \frac{p_- v_-}{\tau} \int_0^\infty G(\eta) H(\eta) c(x + \eta v_-, t - \eta)\, d\eta. \quad (35)$$

If the probability that a particle moves without collision during a time larger than a certain value does not depend on the history of the particle movement, then for arbitrary t_1 and t_2 —because of the independence of the two events—holds $G(t_1 + t_2) = G(t_1)G(t_2)$. From this relation it follows that $G(t) = \exp(-t/\tau)$. For simplicity we assume that the number of particles changes in time according to first-order kinetics, so $H(t) = \exp(-kt)$. We also must take into account that in a coordinate system with no convective flow holds $p_+ v_+ = p_- v_-$, that the net flux is $j = j_+ - j_-$, and that the concentration is $c = j_+/v_+ + j_-/v_-$.

Integrating Eqs. 34 and 35 by parts we transform these integral equations to differential ones:

$$\left(\frac{1}{\tau} + k\right) j_+ = \frac{p_+ v_+}{\tau} c(x, t) - \frac{\partial j_+}{\partial t} - v_+ \frac{\partial j_+}{\partial x}$$

$$\left(\frac{1}{\tau} + k\right) j_- = \frac{p_- v_-}{\tau} c(x, t) - \frac{\partial j_-}{\partial t} + v_- \frac{\partial j_-}{\partial x}.$$

Linear combinations of the last two equations give rise to

$$\frac{\partial c}{\partial t} + \frac{\partial j}{\partial x} + kc = 0 \quad (36)$$

$$(1 + k\tau) j + \tau \frac{\partial j}{\partial t} + \tau (v_+ - v_-) \frac{\partial j}{\partial x} = -\tau v_+ v_- \frac{\partial c}{\partial x}. \quad (37)$$

It is evident that these equations are exactly the same as Eqs. 21 and 22 in a coordinate system moving with the average velocity $\bar{u}$ and for a first-order chemical reaction, except that D_e and u_a have been replaced by $\tau v_+ v_-$ and $v_+ - v_-$. It is noteworthy that Eq. 37 for the diffusion or dispersion flux contains the rate of chemical reaction and is applicable for arbitrary rates of spatial and temporal variations of the average concentration.

The initial and boundary conditions for Eqs. 36 and 37 are the same as for Eqs. 21 and 22. On a particle level of scrutiny, they immediately follow from concentrations or fluxes of particles moving in both directions j_+/v_+ and j_-/v_- at some moment of time or at some point. More general equations can be obtained by the same approach. Such a generalization of Eqs. 36 and 37 will contain more than two particle velocities.

The preceding derivation on the basis of a random walk is not the only way to arrive at Eq. 37 instead of Eq. 31. The work by Davidov (1935), Weiss (1976), Masoliver et al. (1989), Masoliver and Weiss (1991), and Van den Broeck (1990) are examples of other similar random walk approaches leading to hyperbolic transport equations. The just considered scheme has been chosen because of its simplicity and the similarity to the traditional derivation of Ficks' law in the elementary kinetic theory of gases.

Discussion

The foregoing modifications of Taylor's (1953, 1954a) intuitive arguments show that the average concentration and dispersion flux satisfy a quasi-linear hyperbolic system of two first-order equations. Consideration of the problem at a particle level of scrutiny and with finite particle velocities taken into account, also results in equations of the same form. For linear problems, when the source function is explicitly independent of time and coordinate, the two equations can be transformed into a hyperbolic equation of the second order for the average concentration or dispersion flux. The first approach can be considered as a useful procedure for obtaining model equations with specified coefficients for a wide class of problems. The second qualitative approach is more general —it relates not only to the cases where the Taylor dispersion is the main mechanism of longitudinal mixing, it also applies to the examination of an arbitrary motion of particles that are subject to dispersion, for example, dispersion due to the randomness of the stream paths, as in flow through packed beds, for molecular and turbulent diffusion, and for other mechanical mixing mechanisms caused by fluid flow. Further we will discuss the wave model on the basis of Eqs. 21 and 22, keeping in mind that Eqs. 36 and 37 are equivalent to the same.

The salient aspect of the proposed wave model of Eqs. 21 and 22, along with the initial and boundary conditions given by Eqs. 26 and 27, rests in the governing equation for the dispersion flux Eq. 22:

$$(1 + \tau q'(\bar{c}, x, t)) j + \tau \frac{\partial j}{\partial t} + \tau (\bar{u} + u_a) \frac{\partial j}{\partial x} = -D_e \frac{\partial \bar{c}}{\partial x}, \quad (22)$$

instead of the commonly used Fickian form:

$$j = -D_e \frac{\partial \bar{c}}{\partial x}. \tag{38}$$

For the case of no chemical reactions, or $\partial q/\partial c = 0$, the form of constitutive Eq. 22 is not new. After Maxwell (1867) it was demonstrated in many different contexts that such constitutive equations are more exact than the classic, local gradient laws, like the laws of Newton, Fourier, and Fick for viscosity, heat conduction, and diffusion, respectively. All these constitutive equations have the structure of Eq. 22 with $\partial q/\partial c = 0$ and $u_a = 0$, and provide more exact descriptions of momentum transfer in viscoelastic liquids (see Joseph, 1990) and in turbulent flows (see Builtjes, 1977 and Loitsianskii, 1982), for heat transfer in homogeneous media (see Chan et al., 1971 and Ocone and Astarita, 1987), and in heterogeneous media (see Buevich, 1985), for turbulent diffusion of mass and heat (see Luikov, 1966), since all transport processes take place with a finite speed of signal propagation. Hyperbolic equations also have been obtained—on the basis of different approaches—for the description of Taylor-type dispersion processes as alternatives to diffusion-type equations; see Thacker (1976), Maron (1978), Dil'man and Kronberg (1983), and Van den Broeck (1991). For the case of a source term independent of the concentration, Eqs. 21 and 22 with the same coefficients were derived by Smith (1981).

This wave model, as well as other hyperbolic equations obtained before, is more exact than the commonly used dispersion model. The wave model is a natural generalization of the simplest plug-flow model, which also possesses wave properties. It incorporates significant features of longitudinal mixing, retains the important qualitative properties of multidimensional problems and, therefore, effectively removes the conceptual deficiencies of the SDM. The wave model fulfills the physical requirements of a finite speed of signal propagation, of no backmixing for unidirectional flow, and of mass conservation, see Eq. 21. The possibility of formulating two boundary conditions only at the reactor inlet in the case of unidirectional flow is obvious.

Some real systems would require a more refined one-dimensional dispersion model or a two- or three-dimensional model for more precise results, but all obtained results are qualitatively applicable to arbitrary dispersion phenomena. The basic wave law for longitudinal dispersion would still prevail over Fick's law independent of the scale of the phenomena; only molecular diffusion phenomena do not require hyperbolic equations.

Note that the velocity of the second wave is not necessarily positive; it may be negative for some velocity distributions. Such a situation can be encountered in bubble columns, fluidized bed reactors, mechanically agitated columns, and so forth. A detailed study of such reactors is beyond the scope of this article. The advantages of the new wave model over the SDM will be demonstrated in a subsequent article.

Relaxation

The model equations form a hyperbolic system, as often is the case when relaxation phenomena are taken into account. Actually, for the case of no component consumption, Eq. 22 can be rewritten in integral form as

$$j(x,t) = -\frac{D_e}{\tau}\int_0^{\infty} \frac{\partial c[x-(\bar{u}+u_a)t', t-t']}{\partial x} \exp(-t'/\tau)\, dt'. \tag{39}$$

This equation shows that the dispersion flux is determined by the concentration gradient at all the preceding moments of time and at upstream points, with a weight function decreasing exponentially with time. This means there is a fading memory of the dispersion flux; the duration of this memory is characterized by the relaxation time τ. Equation 39 shows that the dispersion flux is not necessarily directed down the gradient of $\bar{c}$ vs. x, because in the previous moments of time and in upstream points the concentration gradient may have had an opposite sign.

Asymmetry

In a coordinate system moving with average velocity, the propagation of the substance forward and backward for most real situations differs under the influence of a velocity profile (see Chatwin, 1970). Equations 21 and 22 take into account this peculiarity of longitudinal dispersion, whereas Eq. 1 is invariant relative to the sign of the longitudinal coordinate in the system moving with the average velocity; the SDM predicts concentration distributions symmetrical in the axial coordinate around the center of gravity of the cloud for a symmetrically injected solute. This noted lack of symmetry is pronounced, for example, in contaminant spreading during a short period for flow through a tube (see Chatwin, 1970 and Yu, 1980).

Physical meaning of the new terms in the constitutive equation

The physical meaning of the terms in Eq. 22 follows from the derivation of the wave model. The dispersion flux, as well as any other characteristic of the nonequilibrium system, is determined by the previous history of the system. This generally obvious fact is not taken into account in Fick's law, but clearly plays a role for a finite particle velocity; see also Eqs. 32 and 39. Therefore, when the dispersion flux at some moment of time and at some point is expressed through the concentration gradient at the same moment of time and at the same point, the changes that occurred in the system in the past must necessarily be present in this relation. The new terms in the constitutive equation characterize such previous changes that influence the concentration gradient. The derivatives of the source term and of the dispersion flux characterize the changes of the concentration gradient due to mass consumption and due to transport of a mass, respectively. The changes due to mass transport consist of two parts: the first part, $\partial j/\partial t + \bar{u}\,\partial j/\partial x$, is determined by simple convective transport, and the second part, $u_a \partial j/\partial x$, characterizes the asymmetry of dispersion phenomena in a coordinate system moving with velocity $\bar{u}$.

Hyperbolicity

The wave model differs principally from the SDM. The second and third terms on the lefthand side of Eq. 22 are important irrespective of their relative magnitude. The presence of these terms changes the type and consequently the qualitative properties of the model equations as well as the boundary conditions for these equations. Formally the SDM follows from Eqs. 21 and 22, when τ and u_a approach zero for a fixed value of D_e. But the parameters of the wave model are not independent for all cases. For unidirectional flow in particular they are interrelated, and Eqs. 21 and 22 remain a hyperbolic system in any case. Hence, the SDM never follows from the more general wave model for unidirectional flow and also cannot be obtained as the exact result from a multidimensional model; it can be justified only as an empirical approximation of more general models in case the solute concentration fields vary slowly in time and space. Also it is an important fact that the rate of component consumption, which is dependent on concentration, enters not only in the mass conservation equation, Eq. 21, but also in the equation for the dispersion flux, Eq. 22.

Model parameters

In comparison to the SDM the wave model contains two additional parameters: the relaxation time τ and the parameter of velocity asymmetry u_a. All three parameters of the wave model can be easily calculated for the case of Taylor dispersion if the velocity profile and the transverse dispersion coefficient are known (see Eqs. 23). The presence of new parameters may seem a complication of the model. But the parameters of the wave model are universal for a given system, because they depend only on flow conditions, geometry, and physical properties. This undoubtedly is to be preferred to the one parameter of the SDM depending on the problem under consideration. The significance of the model parameters and the methods for their experimental determination will be considered in a later article.

Boundary conditions

With the SDM it is difficult to describe the interaction between the system and its surroundings (see Nauman, 1981 and Novy et al., 1990). There are no such difficulties with boundary conditions for the wave model. The possibility of formulating boundary conditions immediately from the multidimensional situation at the inlet is an essential advantage of Eqs. 21 and 22. Another important aspect of the wave model is that boundary conditions have to be specified only at the inlet in the case of unidirectional flows. This simplifies the mathematical problem if compared to the two-point boundary-value problem of Eqs. 1 and 2.

It should be noted that the change in the type of equation inevitably results in a change in the boundary conditions. Transition to a diffusion-type Eq. 1 from a more general multidimensional description inevitably violates the structure of the real feedback, giving rise to a problem of boundary conditions. As a result the boundary conditions for Eq. 1 have to be specified at the inlet and at the outlet of the reactor instead of only at the inlet. But boundary conditions are an integral part of the problem under consideration; in general they are no less important than the model equations themselves. The boundary conditions can be changed only when the solution of the equation is not sensitive to their choice.

It is known that the SDM describes the spread of the concentration after some "forgetting time," when the particles no longer remember their initial position in the cross-sectional area to the flow or their initial longitudinal velocity. Hence specification of the dispersion flux at the inlet or at the outlet of the reactor for the SDM makes no sense, as the specification of its initial value is also senseless. This means that the problem of boundary conditions for a Fickian-type dispersion model is senseless from the physical point of view, and therefore all discussions about Danckwerts' boundary conditions and their modifications are senseless too; only the mass conservation requirement is important for the Fickian dispersion model.

Transverse nonuniformity

The wave model contains two state variables $\bar{c}$ and j, rather than the one variable $\bar{c}$ in the Fickian-type dispersion model. Using just the average concentration for the description of dispersion processes considerably restricts the range of validity of the SDM because, according to its definition and also in the wave model, the dispersion flux is determined specially by the transverse concentration distribution. The SDM is clearly incorrect in certain applications. It does not distinguish between different spatial concentration fields with the same average concentration distribution. For example, if the concentration is not uniform in a cross section of the flow—this depends on coordinates y and/or z—and does not depend on the longitudinal coordinate x, the dispersion flux is not equal to zero due to the nonuniform velocity profile; but there is no gradient in the average concentration, so Eq. 38 indicates a zero dispersion flux. Moreover, it is not difficult to find situations where for Eq. 38 to be correct the dispersion coefficient must be negative. These obvious contradictions are eliminated when Eq. 22 is used instead of Eq. 38. The second state variable j of the wave model—the dispersion flux—permits us to take a transverse concentration distribution into account. In the proposed model the dispersion flux is a measure of the concentration nonuniformities. Despite the occurrence of a second variable the order of the model equations is not increased, just the type of the equations is changed. Being one-dimensional a wave model takes into account the transverse concentration distributions that for Taylor dispersion can be estimated by the use of Eqs. 12 or A14 (see Appendix) if $\bar{c}$ and j are known.

Limits of applicability and possible generalizations of the wave model

The previous treatment of longitudinal dispersion does not specify the region of validity for Eqs. 21 and 22. The significance of the equations depends, of course, on the velocity $u(y, z)$ and the transverse dispersion coefficient $D_t(y, z)$. Some preliminary conclusions about the applicability of the wave model can be drawn in a simple way on the basis of the qualitative derivation of wave equations. Such a derivation shows that Eq. 22 corresponds to a description of dispersion processes with only two dispersion velocities. Both approaches considered may not appear particularly realistic since real particles will obviously have a continuous distribution of their longitudinal velocity. We can expect that the simplest form of the wave model gives a solution to multidimensional convective-diffusion-reactive problems, in which the longitudinal dispersion is dominated by one spatial scale of flow nonuniformities. If more than one scale of flow nonuniformities exerts a comparable influence on longitudinal dispersion, the generalization of the model may be realized by successive application of the transverse averaging procedure for the different spatial scales.

Conclusion of Sundaresan et al. (1980)

The results of the foregoing analysis contradict the main conclusion by Sundaresan et al. (1980), who state the requirement of no backmixing is impossible to meet with models described by second-order partial differential equations. Their conclusion follows from their statement that the second boundary condition at the inlet is not at all obvious from the viewpoint of the physics of the problem. It seems that Sundaresan et al. in considering wave equations were victims of ideas inherent to the diffusion equation. Two inlet boundary conditions relating to the physics of the problem cannot be specified for an SDM, where the concentration and the dispersion flux are interrelated, but they can easily be specified for hyperbolic equations. In particular, the hyperbolic equations discussed by Sundaresan et al. are obtained on the basis of a cells-in-series model; hence, the boundary conditions for that model must also follow from the boundary conditions for a cell model and not from ideas inherent to the SDM. The second boundary condition is obvious if we take into account that the cells consist of a plug-flow section and a well-stirred region: the solution of the problem depends on where in the cells material is introduced. These distributions determine the second boundary condition—the total flux or dispersion flux at the inlet in addition to the inlet concentration.

Mathematical aspects of the used procedure

The mathematical procedure proposed in the first part of this article also can be considered as an approximate method for the solution of some kind of partial differential equations. Briefly, this procedure is as follows.

Function $c^{(i)}$ and $c^{(i+1)}$ $(i = 0, 1, \ldots)$ are successive approximations of the concentration. They involve $i+1$ unknown functions of the time and the longitudinal coordinate, like the average concentration $\bar{c}$ and the dispersion flux j. The problem is to find this function. One equation for finding the unknown functions immediately follows from the solvability condition of the equation for $c^{(i+1)}$. Other equations are obtained from a similar approach, as in the method of weighted residuals (see Finlayson, 1972). If $c^{(i)}$ is the exact solution, the residual $R = c^{(i)} - c^{(i+1)}$ should be zero for all values of the independent variables. According to this method we choose the unknown functions $\bar{c}$, j, … in such a way that the residual is forced to be zero in some weighted-average sense

$$\int_A w_j(y, z) R \, dy \, dz = 0$$

where w_j, $j = 1, 2, \ldots, i$ are weighting functions. Here the velocity $u - \bar{u}$ in a coordinate system moving with the average velocity is used as a weighting function.

The mathematical procedure of obtaining Eqs. 21 and 22 from Eq. 19 can be refined in the case of a nonlinear source term, q, taking into account the transverse concentration distribution for calculating the average consumption rate $\bar{q}$. For this purpose we can use a more exact Taylor series than Eq. A5 (see the Appendix) by adding the second-order term to the expansion of the source term q:

$$q(c, x, t) \approx q(\bar{c}, x, t) + q'(\bar{c})(c - \bar{c}) + \frac{1}{2} q''(\bar{c})(c - \bar{c})^2. \quad (40)$$

Use of Eq. 40 instead of Eq. A5 gives a more refined system of one-dimensional equations:

$$\frac{\partial \bar{c}}{\partial t} + \bar{u}\frac{\partial \bar{c}}{\partial x} + \frac{\partial j}{\partial x} + q(\bar{c}, x, t) + \frac{1}{2} q''(\bar{c}, x, t)\frac{\tau}{D_e} j^2 = 0 \quad (41)$$

$$\left[1 + \tau q'(\bar{c}, x, t) + \frac{1}{2} j \frac{\tau}{v_1} q''(\bar{c}, x, t)\right] j + \tau \frac{\partial j}{\partial t} + \tau(\bar{u} + u_a)\frac{\partial j}{\partial x} = -D_e \frac{\partial \bar{c}}{\partial x}. \quad (42)$$

This system compared to Eqs. 21 and 22 now contains an additional parameter

$$v_1 = \frac{\overline{g_1^2} D_e}{\overline{g_1^3}},$$

with the dimension of velocity. The presence of four parameters in Eqs. 41 and 42 undoubtedly makes their use as a reactor model more difficult.

Conclusions

The main purpose of this article is to prove the necessity of exchanging Fick's law for a Maxwell-type equation for the description of mass-dispersion phenomena; the one-dimensional longitudinal dispersion in chemical reactors is such a case. Based on extensions of two well-known approaches by small but significant modifications, a new wave model for longitudinal dispersion in continuous flow systems has been developed. The obtained model eliminates the conceptual shortcomings inherent to the Fickian dispersion model. The wave model is physically more acceptable than the commonly encountered standard dispersion model. An essential conclusion is that this model described by second-order partial differential equations satisfies the requirements of finite speed of the signal propagation, and it does not necessarily predict the backmixing.

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Notation

A = cross-sectional area perpendicular to the flow
∂A = cross-sectional boundary at the wall
D = dispersion or molecular diffusion coefficient
g_1 = function defined by Eq. 24
$g_{2,3}$ = functions in Eq. 15
$G(\eta)$ = probability that a particle survives a time η without collisions
$H(\eta)$ = probability that a particle does not disappear due to chemical reaction during a time η
L = reactor length
$\mathcal{L}$ = differential operator, $\partial/\partial t + \bar{u}\,\partial/\partial x$
n = number of molecules per unit volume
$\mathbf{n}$ = outward normal
r = radial coordinate
$u_{1,2}$ = characteristic velocities of Eqs. 21 and 22

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Appendix: Derivation of Eqs. 21 and 22

A three-dimensional convective diffusion equation, Eq. 19, is

$$\frac{\partial c}{\partial t}+u(y,z)\frac{\partial c}{\partial x}+q(c,x,t)=\nabla(D_t\nabla c), \qquad \text{(A1)}$$

with boundary conditions

$$D_t\mathbf{n}\nabla c=0 \qquad \text{on} \qquad \partial A. \qquad \text{(A2)}$$

The longitudinal dispersion equation has its origin in the cross-sectionally averaged Eq. A1:

$$\frac{\partial\bar{c}}{\partial t}+\bar{u}\frac{\partial\bar{c}}{\partial x}+\frac{\partial j}{\partial x}+\bar{q}=0 \qquad \text{(A3)}$$

where

$$j=\overline{(u-\bar{u})c} \qquad \text{(A4)}$$

is the dispersion flux due to the velocity shear. The average consumption rate $\bar{q}$ where nonlinear dependence of q on c and the dispersion flux j in Eq. A3 cannot be related directly to $\bar{c}$. If the transverse variations in the concentration are small compared to the mean concentration, however, we can approximate the consumption rate with a one-term Taylor expansion:

$$q(c,x,t)=q(\bar{c},x,t)+q'(\bar{c})(c-\bar{c}) \qquad \text{(A5)}$$

where the prime indicates the derivative with respect to c, $q'=\partial q/\partial c$. In that case,

$$\bar{q}=q(\bar{c},x,t), \qquad \text{(A6)}$$

and the approximation becomes exact if q is a linear function of c. Further we need to obtain an expression for c in terms of $\bar{c}$ and j and their derivatives with respect to time t and longitudinal coordinate x in order to find the constitutive equation for the dispersion flux with the help of Eq. A4. When the transverse variation of the concentration is small—the system is close to equilibrium—we can find a first approximation for the concentration $c^{(1)}$ from Eq. A1, in which some averaged concentration $\overline{c^{(0)}}$ instead of c is used in the left-hand side:

$$\mathfrak{L}\overline{c^{(0)}}+q\left(\overline{c^{(0)}},x,t\right)+(u-\bar{u})\frac{\partial\overline{c^{(0)}}}{\partial x}=\nabla(D_t\nabla c^{(1)}) \qquad \text{(A7)}$$

where $\mathcal{L} = \partial/\partial t + \bar{u}\,\partial/\partial x$. Integrating Eq. A7 over the cross section we find the solvability condition for this equation

$$\mathcal{L}\overline{c^{(0)}} + q\left(\overline{c^{(0)}}, x, t\right) = 0, \qquad \text{(A8)}$$

which corresponds to the plug-flow model. Subtracting Eq. A7 from Eq. A8, we obtain

$$(u - \bar{u})\frac{\partial\overline{c^{(0)}}}{\partial x} = \nabla(D_t\nabla c^{(1)}). \qquad \text{(A9)}$$

The solution of Eq. A9 with the boundary conditions Eq. A2 is

$$c^{(1)} = \overline{c^{(1)}} + g_1(y, z)\frac{\partial\overline{c^{(0)}}}{\partial x} \qquad \text{(A10)}$$

where function g_1 satisfies the equation

$$\nabla(D_t\nabla g_1) = u - \bar{u} \qquad \text{(A11)}$$

with

$$\bar{g}_1 = 0 \quad \text{and} \quad D_t\mathbf{n}\nabla g_1 = 0 \quad \text{on} \quad \partial A. \qquad \text{(A12)}$$

Substituting Eq. A10 into Eq. A4, we find the well-known equation for the dispersion flux:

$$j^{(1)} = -D_e\frac{\partial\overline{c^{(0)}}}{\partial x}; \qquad D_e = -\overline{(u - \bar{u})g_1}. \qquad \text{(A13)}$$

Equations A3, A6, and A13 form the SDM if in addition we suppose that $j^{(1)}$ and $\partial\overline{c^{(0)}}/\partial x$ cannot be distinguished from j and $\partial c/\partial x$. Using Eq. A13, we rewrite Eq. A10 as

$$c^{(1)} = \overline{c^{(1)}} - \frac{g_1(y, z)}{D_e}j^{(1)}. \qquad \text{(A14)}$$

We shall further assume the dispersion flux $j^{(1)}$ to be an unknown variable, which is not obliged to obey Eq. A13.

On substituting Eq. A14 into the lefthand side of Eq. A1, and using Eq. A5, we have the equation for a more accurate concentration distribution $c^{(2)}$:

$$\mathcal{L}\overline{c^{(1)}} - (g_1/D_e)\,\mathcal{L}j^{(1)} + (u - \bar{u})\frac{\partial\overline{c^{(1)}}}{\partial x} - (u - \bar{u})(g_1/D_e)\frac{\partial j^{(1)}}{\partial x} + q\left(\overline{c^{(1)}}, x, t\right) - q'\left(\overline{c^{(1)}}, x, t\right)(g_1/D_e)j^{(1)} = \nabla(D_t\nabla c^{(2)}). \qquad \text{(A15)}$$

Averaging Eq. A15 over the cross section, we obtain:

$$\mathcal{L}\overline{c^{(1)}} + \frac{\partial j^{(1)}}{\partial x} + q\left(\overline{c^{(1)}}, x, t\right) = 0, \qquad \text{(A16)}$$

which in first approximation is the mass conservation equation. Subtracting Eq. A16 from Eq. A15, we obtain

$$-(g_1/D_e)\,\mathcal{L}j^{(1)} + (u - \bar{u})\frac{\partial\overline{c^{(1)}}}{\partial x} - [1 + (u - \bar{u})(g_1/D_e)]\frac{\partial j^{(1)}}{\partial x} - q'\left(\overline{c^{(1)}}, x, t\right)(g_1/D_e)j^{(1)} = \nabla(D_t\nabla c^{(2)}). \qquad \text{(A17)}$$

The solution of Eq. A17 with the boundary conditions, Eq. A2 is

$$c^{(2)} = \overline{c^{(2)}} + g_1(y, z)\frac{\partial\overline{c^{(1)}}}{\partial x} - g_2(y, z)\left[\mathcal{L}j^{(1)} + q'\left(\overline{c^{(1)}}, x, t\right)j^{(1)}\right] - g_3(y, z)\frac{\partial j^{(1)}}{\partial x} \qquad \text{(A18)}$$

where the functions $g_2(y, z)$ and $g_3(y, z)$ satisfy the equations

$$\nabla(D_t\nabla g_2) = g_1/D_e \qquad \text{(A19)}$$

$$\nabla(D_t\nabla g_3) = 1 + (u - \bar{u})g_1/D_e \qquad \text{(A20)}$$

with

$$\bar{g}_1 = 0 \quad \text{and} \quad D_t\mathbf{n}\nabla g_i = 0 \quad \text{on} \quad \partial A \quad \text{and} \quad i = 2, 3. \qquad \text{(A21)}$$

Substituting Eq. A18 into Eq. A4, we find the constitutive equation for the dispersion flux:

$$j^{(2)} + \tau\left[\mathcal{L}j^{(1)} + q'\left(\overline{c^{(1)}}, x, t\right)j^{(1)} + u_a\frac{\partial j^{(1)}}{\partial x}\right] = -D_e\frac{\partial\overline{c^{(1)}}}{\partial x} \qquad \text{(A22)}$$

where $\tau = \overline{g_2(u - \bar{u})}$ is a constant with the dimension of time and $u_a = \overline{g_3(u - \bar{u})}/\tau$ is a constant with the dimension of velocity. If we assume that $\overline{c^{(1)}} \approx \bar{c}$ and $j^{(1)} \approx j^{(2)} \approx \bar{j}$, from Eqs. A16 and A22 we get one-dimensional equations, which are more general than the plug-flow model:

$$\frac{\partial\bar{c}}{\partial t} + \bar{u}\frac{\partial\bar{c}}{\partial x} + \frac{\partial j}{\partial x} + q(\bar{c}, x, t) = 0 \qquad \text{(A23)}$$

$$(1 + \tau q'(\bar{c}, x, t))j + \tau\frac{\partial j}{\partial t} + \tau(\bar{u} + u_a)\frac{\partial j}{\partial x} = -D_e\frac{\partial\bar{c}}{\partial x}. \qquad \text{(A24)}$$

The solutions to Eqs. A11, A19, and A20 in general can be obtained through the eigenfunctions $f_i(y, z)$ of the eigenvalue problem:

$$\nabla(D_t\nabla f_i) + \mu_i f_i = 0$$

$$D_t\mathbf{n}\nabla f_i = 0 \quad \text{on} \quad \partial A, \qquad \text{(A25)}$$

which is assumed to possess a discrete set of eigenvalues $\mu_i > 0$ ($i = 1, 2, \ldots$) and the corresponding eigenfunctions f_i ($i = 1, 2, \ldots$). The eigenfunctions are orthogonal and normalized:

$$\bar{f}_i = 0, \qquad \overline{f_i f_j} = \begin{cases} 1 & i = j \\ 0 & i \neq j. \end{cases}$$

The solution for g_1 can be written in terms of eigenfunctions as

$$g_1 = \sum_{i=1}^{\infty} \frac{\beta_i}{\mu_i} f_i, \qquad \beta_i = \overline{(\bar{u} - u) f_i} \tag{A26}$$

and

$$D_e = -\overline{(u - \bar{u}) g_1} = \sum_{i=1}^{\infty} \frac{\beta_i^2}{\mu_i}. \tag{A27}$$

It is not necessary to solve Eqs. A19 and A20 to find τ and u_a. On multiplying these equations by g_1 and integrating over the cross section, we find, after accounting for the relationship

$$\overline{g_1 \nabla (D_t \nabla g_i)} = -\overline{D_t \nabla g_1 \nabla g_i} = \overline{g_i \nabla (D_t \nabla g_1)} = \overline{g_i (u - \bar{u})} \qquad i = 2, 3,$$

that

$$\tau = \frac{\overline{g_1^2}}{D_e}; \qquad u_a = \frac{\overline{(u - \bar{u}) g_1^2}}{D_e \tau}. \tag{A28}$$

Equations A27 and A28 show that for arbitrary nonuniform flow $D_e > 0$ and $\tau > 0$.

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