LONGITUDINAL DISPERSION IN THE FLOW OF A MULTICOMPONENT
MIXTURE IN A PLANE CHANNEL

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The propagation of a multicomponent mixture in a channel is considered. An equation generalizing the well-known Taylor equation [1] both to the multicomponent case and so as to take account of the dependence of the transport coefficients on the concentrations of the components is obtained.

In analyzing numerous problems associated with liquid flow in channels, the model of impurity dispersion is widely used. The basic advantage of this model is the significant simplification of the mass- and heat-transfer equations — more precisely, the replacement of a three-dimensional equation containing a convective term which depends on the coordinate transverse to the flow by a two-dimensional equation (averaged over this coordinate) which contains only constant coefficients in the simplest cases. This transformation was first undertaken in [1]. Subsequent intensive research in this area led to the proposal of several original approaches to the refinement and development of the theory for more complex situations; see [2-7], for example.

In [1-7] and elsewhere, only one equation of convective diffusion was considered, whereas problems in which the mixture contains several components or the influence of thermodiffusion and other effects must be taken into account are not uncommon in practice. An example here is the problem of liquid capillary chromatography, in which the action of thermodiffusion on mass dispersion processes in investigated [8]. In [8], however, the temperature profile was known in advance, i.e., no account was taken of the influence of variation in concentration gradients of the material on the heat transfer, as is required by the thermodynamic equations of irreversible processes and, in particular, the Onsager reciprocity principle [9]. Thus, in [8], again, one equation for the concentration of the material was essentially dealt with.

Generalization of the model of [1] to the multicomponent case was considered in [10], where the dispersion in a circular tube with a first-order reaction at the wall was investigated. However, a series of interesting questions — such as the degree to which the dispersion coefficients satisfy the principles of nonequilibrium thermodynamics, the possibility of a nonlinear dependence of the diffusion coefficients on the concentration of the components, etc. — was ignored.

The basic equations of the problem may be written in matrix form as follows

$$\varepsilon^2 \frac{\partial C}{\partial t} + \varepsilon \left(\frac{1}{3} - y^2 \right) \frac{\partial C}{\partial x} = \frac{\partial}{\partial y} \left(L \frac{\partial C}{\partial y} \right), \tag{1}$$

where all the quantities are dimensionless and the investigation is undertaken in a coordinate system moving at the mean velocity. Since the fundamental aspects of the method used below [7] do not depend on the form of the prismatic-channel cross section and the results obtained are analogous, but more unwieldy, analysis is restricted here to dispersion in a plane channel, the velocity profile in which is described by the usual Poiseuille parabola $v(Y) = u(1 - Y^2/h^2)$. Taking the Poiseuille velocity profile, the material being transferred is assumed to be dynamically passive, exerting no influence on the liquid flow, which is characteristic of homogeneous mixtures.

In Eq. (1), the term $\partial(L\partial C/\partial x)/\partial x$ is neglected in comparison with $\partial(L\partial C/\partial y)\partial y$, which is valid if the channel is sufficiently extended. The dimensionless parameters in this equation are related to dimensional parameters as follows: $x = X/\ell$, $y = Y/h$, $t = \tau h^2 u^2/(D_* \ell^2)$, $\varepsilon = uh^2/(\ell D_*)$, where D_* is the characteristic value of the diffusion coefficients; τ, X, Y, are

the dimensional time and coordinates; ℓ is the length scale along the channel, which is determined from the character of the variation in the vector of the specified initial concentration along the x axis

$$C|_{t=0} = C_* (x, y), \quad x \in (-\infty, +\infty). \tag{2}$$

The matrix L has components L_{ij} which are symmetric $L_{ij} = L_{ji}$ and positive-definite, as required by the Onsager reciprocity relations and the principle of increasing entropy [9]. In addition, L_{ij} are assumed to depend on the components c_i of column matrix C, one component of which (where necessary) may be regarded as the temperature. This means that both the initial system in Eq. (1) and the simplified systems found below are nonlinear.

To Eq. (1) are added the boundary conditions

$$L \frac{\partial C}{\partial y} = 0 \quad \text{when} \quad y = \pm 1, \tag{3}$$

which are adequate for the present purposes. These conditions (n of them with respect to the number of components) express the absence of a mass flux through the channel boundary.

The solution of Eq. (1) is sought using the perturbation method [11, 12], in the form of a series in powers of the small parameter ε. This procedure is essentially equivalent to the method of successive approximation [1], but it does not include semintuitive steps [1] and is not only better suited to finding corrections but also clearer. Substituting the series

$$C = C_0 + \varepsilon C_1 + \varepsilon^2 C_2 + \cdots \tag{4}$$

into Eq. (1) and grouping terms of the same order in ε, the following equations are obtained

$$\frac{\partial}{\partial y} \left[L(C_0) \frac{\partial C_0}{\partial y} \right] = 0, \tag{5}$$

$$\frac{\partial}{\partial y} \left[L(C_0) \frac{\partial C_1}{\partial y} + L'(C_0) C_1 \frac{\partial C_0}{\partial y} \right] = \left(\frac{1}{3} - y^2 \right) \frac{\partial C_0}{\partial x}, \tag{6}$$

$$\frac{\partial}{\partial y} \left\{ L(C_0) \frac{\partial C_2}{\partial y} + L'(C_0) C_1 \frac{\partial C_1}{\partial y} + \left[L'(C_0) C_2 + \frac{L''(C_0)}{2} C_1^2 \right] \frac{\partial C_0}{\partial y} \right\} = \left(\frac{1}{3} - y^2 \right) \frac{\partial C_1}{\partial x} + \frac{\partial C_0}{\partial t} \tag{7}$$

and so on. The boundary conditions are written in the form

$$L(C_0) \frac{\partial C_0}{\partial y} = 0, \quad L(C_0) \frac{\partial C_1}{\partial y} + L'(C_0) C_1 \frac{\partial C_0}{\partial y} = 0,$$

$$L(C_0) \frac{\partial C_2}{\partial y} + L'(C_0) C_1 \frac{\partial C_1}{\partial y} + \left[L'(C_0) C_2 + \frac{L''(C_0)}{2} C_1^2 \right] \frac{\partial C_0}{\partial y} = 0$$

$$\text{when} \quad y = \pm 1. \tag{8}$$

Here the derivative of the matrix L is combined with the vectors C_i as a tensor with the components $L'_{ijk} = \partial L_{ij}/\partial c_k$. For the sake of brevity, the dependence of L on C_0 is omitted below.

Integrating Eq. (5) once, and taking account of the corresponding condition in Eq. (8), it is found that $L \partial C_0/\partial y = 0$; hence, in view of the nondegeneracy of the matrix L, it follows that $\partial C_0/\partial y = 0$, and this leads to the conclusion that C_0 depends only on x and t, i.e., $C_0 = G(x, t)$. The same procedure applied to Eq. (6), taking account of the data obtained on C_0, gives

$$C_1 = L^{-1} \frac{\partial G}{\partial x} \left(\frac{y^2}{6} - \frac{y^4}{12} \right) + F(x, t), \tag{9}$$

where the column matrices G and F have yet to be determined. To obtain the equation satisfied by the matrix function G it is sufficient to integrate Eq. (7) with respect to y over

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the limits (-1, 1). Then, using the corresponding relation of Eq. (8), it is found that

$$\frac{\partial G}{\partial t} = \frac{8}{945} \frac{\partial}{\partial x} \left(L^{-1} \frac{\partial G}{\partial x} \right),$$ (10)

which is the desired dispersion equation, known previously only for the case L = const. Note that, in view of the properties of matrix L (that it is symmetric and positive-definite), the inverse matrix L^{-1} will have precisely the same properties, i.e., the system in Eq. (10) satisfies the same principles of nonequilibrium thermodynamics as the initial Eq. (1), but is significantly simpler.

Continuing the given procedure, an equation for F is obtained after certain computations

$$\frac{\partial F}{\partial t} - \frac{8}{945} \frac{\partial}{\partial x} \left(L^{-1} \frac{\partial F}{\partial x} \right) + \frac{8}{945} \frac{\partial}{\partial x} \left(L^{-1} L' F L^{-1} \frac{\partial G}{\partial x} \right) =$$

$$= \frac{3353}{5580} \frac{\partial}{\partial x} \left(L^{-1} \frac{\partial G}{\partial t} \right) - \frac{7}{180} \frac{\partial}{\partial t} \left(L^{-1} \frac{\partial G}{\partial x} \right) - \frac{34}{93555} \frac{\partial}{\partial x} \left[L^{-1} L' \left(L^{-1} \frac{\partial G}{\partial x} \right)^2 \right].$$ (11)

Thus, Eqs. (10) and (11) are obtained for the vector functions of the first two approximations C_0 and C_1. As is evident from Eqs. (5)-(7), the desired functions do not contain derivatives with respect to the time. This indicates that the initial problem is singularly perturbed [11, 12], and "internal" coordinates must be introduced for its detailed description. In this case, it is assumed that $T = t/\varepsilon^2$ is the internal time. Finding the solution of the internal problem, as before, in the form of a solution analogous to Eq. (4), the equation for the zero-approximation function is obtained

$$\frac{\partial C_0^*}{\partial T} = \frac{\partial}{\partial y} \left[L (C_0^*) \frac{\partial C_0^*}{\partial y} \right],$$ (12)

where an asterisk denotes terms of the internal expansion. The basic problem is now to obtain the initial conditions for the equations of the external problem — Eqs. (10) and (11). As will be evident from what follows, there is no need to solve Eq. (12) with the condition in Eq. (2) in order to find G(x, 0). In the linear case L = const, it is also simple to find the initial condition for the vector function F; in the nonlinear case $L = L(C_0^*)$, the condition for F is expressed in terms of the vector C_0^*, which must be found from Eq. (12).

Writing Eq. (1) in the internal variables $T = t/\varepsilon^2$, x, y and integrating it with respect to y over the ilmits (-1, 1), the following relation is obtained in the zero approximation with respect to ε

$$\frac{\partial}{\partial T} \int_{-1}^{1} C_0^* dy = 0 \Rightarrow \int_{-1}^{1} C_0^* dy = \int_{-1}^{1} C_* (x, y) dy,$$ (13)

and hence, after passing to the limit $T \to \infty$, using the principle of matching in the limit [11, 12]

$$\lim_{T \to \infty} C_0^* = \lim_{t \to 0} C_0$$ (14)

the desired initial condition is determined

$$G (x, 0) = \frac{1}{2} \int_{-1}^{1} C_* (x, y) dy,$$ (15)

as could have been predicted on the basis of intuitive considerations. To obtain the conditions for Eq. (11), a relation of the order of ε following from Eq. (1) is written

$$\frac{\partial}{\partial T} \int_{-1}^{1} C_1^* dy + \frac{\partial}{\partial x} \int_{-1}^{1} \left(\frac{1}{3} - y^2 \right) C_0^* dy = 0.$$ (16)

After some manipulations, it may be reduced to the form

$$\frac{\partial}{\partial T} \int_{-1}^{1} C_1^* dy + \frac{\partial}{\partial x} \left\{ \frac{1}{6} \int_{-1}^{1} \left(y^2 - \frac{y^4}{2} \right) \left[L^{-1} \frac{\partial C_0^*}{\partial T} - L^{-1}L' \left(\frac{\partial C_0^*}{\partial y} \right)^2 \right] dy \right\} = 0. \tag{17}$$

Assuming L = const, it is simple to integrate Eq. (17) over time, with the result ($C_1^* = 0$ when T = 0)

$$\int_{-1}^{1} C_1^* \, dy + \frac{\partial}{\partial x} \left[\frac{L^{-1}}{6} \int_{-1}^{1} \left(y^2 - \frac{y^4}{2} \right) (C_0^* - C_*) \, dy \right] = 0. \tag{18}$$

Since the "deformation" $t = T\varepsilon^2$ of the time includes the factor ε^2, the matching principle in Eq. (14) may also be applied to C_1^* and C_1. Hence, using Eq. (9), the desired initial condition for F is found

$$F(x, 0) = \frac{L^{-1}}{12} \frac{\partial}{\partial x} \int_{-1}^{1} \left(y^2 - \frac{y^4}{2} - \frac{7}{15} \right) C_*(x, y) \, dy. \tag{19}$$

In the general case, with a dependence of L on C, the following equation for the vector function F may be proposed

$$F(x, 0) = \frac{1}{2} \frac{\partial}{\partial x} \int_{-1}^{1} \left(\frac{1}{3} - y^2 \right) dy \int_{0}^{\infty} [G(x, 0) - C_0^*] \, dT - \frac{7}{180} L^{-1} \frac{\partial G(x, 0)}{\partial x}, \tag{20}$$

where an integral characteristic of the solution of the problem in Eqs. (12), (2), and (3) is required to calculate F(x, 0).

In describing dispersional phenomena, the behavior of the concentration of the materials at sufficiently large times is basically of interest, i.e., the external solution in the given formulation. It is precisely at large times that the dispersion equation is applicable, as proven repeatedly in the literature, both by various estimates [2, 3, 6] and by asymptotic analysis of the accurate solution for the problem of the propagation of material in a circular tube [13]. Nevertheless, it has been estabished [6, 14] that, when chemical reactions occur in the flow, the solution of the dispersion equations may give significant deviations from the solutions obtained on the basis of the complete equations. To "expand" the applicabiity of dispersion theory, equations of hyperbolic type which depend (within known limits) on their method of derivation are proposed [5, 6]. Consideration of specific examples shows the adequacy of equations of hyperbolic type, and the closeness of their solutions at large times to the solutions of the diffusional model of the type in Eq. (10) in those cases where there are no chemical reactions of great intensity. On the basis of the equations obtained for the two approximations in Eqs. (10) and (11), an equation for the mean concentration may be formulated, with an accuracy up to terms of order ε. This will be done here only in the linear case L = const.

Integrating Eq. (4) with respect to y over the limits (−1, 1) and taking account of Eq. (9), the following expression is obtained for the mean concentration

$$\langle C \rangle = \frac{1}{2} \int_{-1}^{1} C dy = G + \varepsilon \left(F + \frac{7}{180} L^{-1} \frac{\partial G}{\partial x} \right) + \cdots \tag{21}$$

with an accuracy to terms of order ε; hence, combining the equations for G and F, the desired equation for the mean concentration over the cross section <C> is obtained

$$\frac{\partial \langle C \rangle}{\partial t} = L^{-1} \left[\frac{8}{945} \frac{\partial^2 \langle C \rangle}{\partial x^2} + \varepsilon \frac{784}{1395} \frac{\partial^2 \langle C \rangle}{\partial x \partial t} \right]. \tag{22}$$

With an accuracy up to terms of order ε, this equation may be given the form of a linearized Korteweg–de Vries–Burgers matrix equation [15], on the basis that in terms of order ε it is correct to replace <C> by G and conversely. Using Eq. (10), the desired equation is obtained

$$\frac{\partial \langle C \rangle}{\partial t} = \frac{8}{945} L^{-1} \left[\frac{\partial^2 \langle C \rangle}{\partial x^2} + \varepsilon \frac{784}{1395} L^{-1} \frac{\partial^3 \langle C \rangle}{\partial x^3} \right], \tag{23}$$

resembling in structure a segment of the expansion of the general dispersion equation of [3]. Remember that the dispersion Eqs. (10), (11), (22), and (23) obtained are written in a moving coordinate system. The system in Eq. (22) has two characteristics

$$x = \text{const}, \quad \varepsilon x - \frac{31}{2058} t = \text{const}, \tag{24}$$

defined in the moving coordinate system for all components $\langle c_i \rangle$; this corresponds to a hyperbolic system when $n = 1$. When $n > 1$, the behavior of Eq. (22) is similar to hyperbolic according to the classication of [15].

Note, in conclusion, that if diffusional transport in the x direction is taken into account as well as the dispersion coefficient $8L^{-1}/945$, as was done in [2, 4], the following formula is obtained

$$D_0 = \frac{8 \mathscr{L}^{-1} h^2 u^2}{945} + \mathscr{L}, \quad \mathscr{L} = D_* L, \tag{25}$$

this expression generalizing the Aris formula [2] in the "plane" variant to the multicomponent case, is written in terms of dimensional parameters.

NOTATION

C, column matrix of the concentration of the components; h, halfwidth of the channel; $G(x, t)$, vector function of first approximation with respect to ε; $F(x, t)$, basic unknown term in the vector function of the second approximation of C with respect to ε; L, matrix of kinetic coefficients; u, maximum liquid velocity in channel; ε, small parameter; $\langle \ \rangle$, symbol of averaging.

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