A Series Solution for Mass Transfer in Laminar Flow with Surface Reaction

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We present an explicit analytical solution for the Lévêque's problem with the boundary condition of the third kind. This solution is applicable to problems of mass (heat) transfer with surface reaction (surface resistance) in the entry region of fully developed flow fields of power law fluids, and to the developing boundary layer flows that admit Falkner-Skan solutions, provided that the Schmidt (Prandtl) number is large. The series form of the solution developed by inversion of the Laplace transform has excellent convergence properties within the concentration (temperature) boundary layer in contrast to the integral forms that are usually reported for problems of this type. An efficient computational algorithm for evaluation of the surface concentration is presented, as well as accurate approximate formulas in the form of simple algebraic expressions for the local and average mass (heat) transfer coefficients and the surface concentration (temperature).

Introduction

Problems of mass or heat transfer between a fluid flowing past a solid surface and the surface arise often in chemical engineering. Examples are heat and mass transfer in liquid films, pipe flow, and boundary layer flow around solid objects. Such a problem can often be approximated well by a simplified form that takes into account only convection parallel to the surface and diffusion in the perpendicular direction. Furthermore, when the shear stress can be assumed constant, the distribution of concentration or temperature is described by the following partial differential equation:

$$y\frac{\partial c}{\partial x}=\frac{\partial^2 c}{\partial y^2}. \tag{1}$$

c denotes dimensionless temperature or concentration, and x and y dimensionless coordinates in the flow direction and the perpendicular direction, respectively. This equation is known as the Lévêque's problem, and it represents the dimensionless form of many different cases of heat or mass transfer under the assumptions noted above. Examples of most practical importance are discussed later on.

When the boundary condition of the first or the second kind is specified at the solid surface ($y=0$), Eq. 1 has well-known solutions in terms of the incomplete gamma function of the variable $\zeta=y^3/(9x)$ (Bird et al., 1960). However, when the boundary condition of the third kind is specified, the solution is much more complicated. In this study, we consider that case, given by Eq. 1 and the boundary conditions:

$$x=0,\ 0\le y<\infty:\quad c=1, \tag{2a}$$

$$0<x<\infty,\ y=0:\quad \frac{\partial c}{\partial y}=D\,c, \tag{2b}$$

$$0<x<\infty,\ y\rightarrow\infty:\quad c=1. \tag{2c}$$

This notation implies a mass transfer problem resulting from a reversible or irreversible surface reaction of the first order whose rate constant is contained in the Damköhler number D. Then, c denotes the dimensionless concentration $(C-C_e)/(C_0-C_e)$, where C is the unknown concentration at the point (x, y), C_e the equilibrium concentration, and C_0 the value of C at $x=0$. This problem describes also heat transfer between the fluid and a thermostated medium beyond a partition at $y=0$. In that case, D should be replaced by the Biot number for heat transfer, C_e by the temperature of the external medium, and concentrations C and C_0 by the corresponding temperatures. For brevity, we refer to the function $c(x, y)$ as to the concentration distribution.

Previous Work

So far, the solution to the problem (Eqs. 1-2c) has been reported only in the form of integrals arising from the inversion of its Laplace transform by contour integration or by the convolution theorem. Apelblat (1980), Friedman (1976), and Ghez (1978) presented the following integral for the concentration at the surface:

$$c(x,0)=\frac{3^{3/2}}{2\pi}\int_0^{\infty}\frac{e^{-(a^3x)z^3}}{z^2+z+1}\,dz, \tag{3}$$

where a denotes a scaled Damköhler number defined in the Notation section. For the full solution, Apelblat (1980) reported the contour integral of the form:

$$c(x,y)=\frac{3^{5/3}\Gamma\left(\frac{2}{3}\right)}{4\pi}\times a\int_0^{\infty}\frac{e^{-zx}}{z}\,\frac{\sqrt{3}(z+a)Ai(-zy)-(z-a)Bi(-zy)}{z^2+az+a^2}\,dz, \tag{4}$$

and Ghez (1978) presented a convolution integral that can be reduced to:

$$c(x,y)=\frac{\gamma\left(\frac{1}{3},\zeta\right)}{\Gamma\left(\frac{1}{3}\right)}+\frac{1}{\Gamma\left(\frac{1}{3}\right)}\int_{\zeta}^{\infty}e^{-z}z^{1/3-1}c(z-\zeta,\,0)\,dz. \tag{5}$$

Here, Ai and Bi denote the two linearly-independent solutions of the Airy differential equation. In addition, Friedman (1976) and Ghez (1978) gave approximate formulas for the surface concentration for small and large values of x, and Ghez (1978) reported the entire concentration field for the reactant and the product of a reversible first-order surface reaction.

Den Hartog and Beek (1968) gave an analytical solution for the average mass transfer coefficient for the case of a reversible first-order surface reaction. The form which they reported is the integral representation of the incomplete gamma function. This solution, however, is the integral of the surface concentration, rather than the function itself, and it was obtained by the method of integral equations, usually applied to the more general problem of mass transfer in hydrodynamic boundary layers (see Lighthill, 1950; Chambré, 1956).

Although integrals (Eqs. 3–5) exist for all values of x and y, a closed form solution would be preferred, at least for the surface concentration, which is of most importance. A practical reason for looking for a different form of the solution is that the integrals in Eqs. 4 and 5 converge slowly for the values of the arguments corresponding to the points inside the concentration boundary layer. Furthermore, Eqs. 1–2c remain the only case of the Lévêque's problem that has no solution in terms of standard mathematical functions. Such a solution would be interesting from a purely mathematical standpoint.

Here, we develop a solution of this problem in the form of a quickly convergent series of well-known functions.

Solution

First taking the Laplace transform of Eqs. 1–2c with respect to x and then introducing the independent variable $t=s^{1/3}y$ results in the following differential equation for the transform $\bar{c}$ $[\bar{c}(s,y)=\int_0^{\infty}e^{-sx}c(x,y)dx]$:

$$\bar{c}_{tt}-t\bar{c}=-\frac{t}{s}, \tag{6}$$

$$t=0:\quad s^{1/3}\bar{c}_t=D\,\bar{c}, \tag{7a}$$

$$t\rightarrow\infty:\quad \bar{c}=\frac{1}{s}. \tag{7b}$$

The homogeneous part of Eq. 6 is the Airy's differential equation, whose general solution is $K_1Ai(t)+K_2Bi(t)$ (Abramovitz and Stegun, 1970, p. 446). The particular solution of Eq. 6 is $1/s$. Therefore, by imposing the boundary conditions 7a–7b on the general solution $\bar{c}=K_1Ai(t)+K_2Bi(t)+1/s$, we obtain:

$$\bar{c}(s,y)=\frac{1}{s}-\frac{a}{c_1}\frac{Ai(s^{1/3}y)}{s(a+s^{1/3})}, \tag{8}$$

where we write t again as $s^{1/3}y$. a denotes the scaled Damköhler number, d_1Da/d_2, where $d_1=Ai(0)$ and $d_2=-Ai'(0)$. The Laplace transform of the surface concentration is obtained by setting $y=0$ in Eq. 8:

$$\bar{c}(s,0)=\frac{s^{1/3}}{s(a+s^{1/3})}. \tag{9}$$

Surface concentration

We shall show later that the only form of solution for the surface concentration reported so far, expression 3, represents a contour integral of expression 9. However, a closed form for the surface concentration is possible if Eq. 9 is rearranged. Introducing the change of variables $p=s/a^3$ and multiplying the numerator and denominator of the resulting fraction by $(p^{2/3}-p^{1/3}+1)$ gives:

$$\bar{F}_0(p)\equiv a^3\bar{c}(s,0)=\frac{1}{p+1}-\frac{p^{-1/3}}{p+1}+\frac{p^{-2/3}}{p+1}. \tag{10}$$

Because $a^3\bar{c}(s,0)$ is a function only of p, the original of $\bar{c}(s,0)$, obtained by inversion with respect to s, is a function only of a^3x. The same function is also the inverse of $\bar{F}_0(p)$ with respect to p, and we obtain it by inverting the righthand side of Eq. 10 term by term. The last two terms are a standard entry in tables of Laplace transforms (e.g., Erdélyi 1954, p. 238), and inversion of the first term is trivial. We find:

$$F_0(\xi)\equiv c(x,0)=e^{-\xi}\left[1+\frac{\gamma\left(\frac{1}{3},-\xi\right)}{\Gamma\left(\frac{1}{3}\right)}+\frac{\gamma\left(\frac{2}{3},-\xi\right)}{\Gamma\left(\frac{2}{3}\right)}\right], \tag{11}$$

where by ξ we denote the scaled variable x:

$$\xi = a^3 x = \frac{1}{3}\left[\frac{\Gamma\left(\frac{1}{3}\right)}{\Gamma\left(\frac{2}{3}\right)}\right]^3 D^3 x = 2.581056543\cdots D^3 x. \qquad (12)$$

Full solution by contour integration

According to the inversion theorem the original $c(x, y)$ is the following contour integral in the complex s-plane:

$$c(x,y) = \frac{1}{2\pi i}\lim_{R\to\infty}\int_{s_0-Ri}^{s_0+Ri} e^{sx}\bar{c}(s,y)ds. \qquad (13)$$

The function $\bar{c}(s,y)$, Eq. 8, has a branch point at $s = 0$ and a pole at $s = -a^3$. Therefore, the integration contour, called the first Bromwich path, is any vertical line in the complex plane extending from $-\infty$ to ∞ with a positive abscissa s_0. To evaluate this integral we consider the integral of $e^{sx}\bar{c}$ over the simply connected curve $ABCDEFA$ shown in Figure 1a.

The line AB is a vertical through s_0, BC and FA are arcs of the semicircle of radius R centered at the point $(s_0, 0)$, and ED is a circle of any radius r smaller than s_0. We choose the negative real axis to represent the branch cut, so that the function $e^{sx}\bar{c}$ is single-valued and without poles on or inside of the contour $ABCDEFA$. Therefore, its integral over this contour is zero.

Next, we consider the contribution of each section of the contour to this integral in the limit as R tends to infinity, remembering that the integral remains zero. The function $Ai(s^{1/3}y)$ in expression 8 tends to zero uniformly with respect to $\arg(s)$ as $|s|$ tends to infinity, and the same is true of $\bar{c}$. Then, the integral of $e^{sx}\bar{c}$ along the arcs BC and FA is zero as well according to Jordan's lemma (see, for example, Le Page, 1961, pp. 259, 323). The integral along the line AB is, therefore, balanced by the integral along the keyhole contour $CDEF$, but as R tends to infinity, the line AB becomes the first Bromwich path, and we have:

$$\frac{1}{2\pi i}\int_{Br} e^{sx}\bar{c}ds + \frac{1}{2\pi i}\lim_{R\to\infty}\int_{CDEF} e^{sx}\bar{c}ds = 0. \qquad (14)$$

Br denotes the first Bromwich path, and the first integral is the same one as in Eq. 13. Let now w denote the contour $CDEF$ in the limit as R tends to infinity and with the reversed sense of integration. With this notation and by combining Eqs. 13 and 14, we obtain:

$$c(x,y) = \frac{1}{2\pi i}\int_{w} e^{sx}\bar{c}(s,y)ds. \qquad (15)$$

Contour w is the second or equivalent Bromwich path. It follows from Cauchy's integral theorem that the above formula holds regardless of the shape of contour w as long as it contains no point of the negative real axis. For example, radius r is an arbitrary finite number, and it is only for the convenience of having a real integral with a simpler form that r is let to tend to zero. Then, the integral in Eq. 15 assumes the form of Eq. 4 for general values of y and the form of Eq. 5 at $y = 0$.

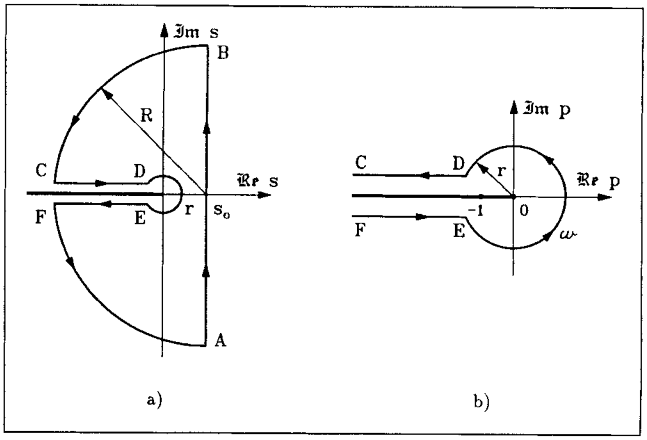

Figure 1. a) A closed contour in the *s*-plane; b) second Bromwich path in the complex *p*-plane.

In the limit as R tends to infinity, the line AB becomes the first and contour the $FEDC$ the second Bromwich path.

In the general case, the shape of the contour w can be changed to fit the problem at hand, and indeed, the method of integration (see sections on the "Deformation of the Path in Complex Inversion Integrals" in Doetsch, 1950). Contour w as shown in Figure 1a is already shaped to fit the purpose of our inversion as presented subsequently.

Series solution

By changing again the variable s to a^3p in expression 8, we obtain a simpler form:

$$\bar{F}(p,\eta) \equiv a^3\bar{c}(s,y) = \frac{1}{p} - \frac{1}{d_1}\frac{Ai(p^{1/3}\eta)}{p(1+p^{1/3})}, \qquad (16)$$

with $\eta = ay$, which states that inversion is to be performed with respect to the complex variable p and that the original F is a function of ξ and η. Next, we represent $Ai(p^{1/3}\eta)$ by the Taylor series of the Airy function given in Table 1. The following expression for $\bar{F}(p, \eta)$ is obtained by grouping the terms of the resulting series according to whether they are analytic functions of p:

$$\bar{F}(p, \eta) = \frac{1}{d_1}\sum_{m=0}^{\infty} t_m(-\eta)\bar{F}_m(p) - \bar{N}(p). \qquad (17)$$

Table 1. Taylor Expansion of the Airy Function*

$$Ai(z) = \sum_{m=0}^{\infty} t_m(z) = \sum_{m=0}^{\infty}(d_1\alpha_m z^{3m} - d_2\beta_m z^{3m+1})$$

$$\alpha_m = \frac{\Gamma\left(\frac{1}{3}+m\right)}{\Gamma\left(\frac{1}{3}\right)}\frac{3^m}{(3m)!}, \quad \beta_m = \frac{\Gamma\left(\frac{2}{3}+m\right)}{\Gamma\left(\frac{2}{3}\right)}\frac{3^m}{(3m+1)!}$$

$$d_1 = Ai(0) = \frac{3^{-2/3}}{\Gamma\left(\frac{2}{3}\right)}, \qquad d_2 = -Ai'(0) = \frac{3^{-1/3}}{\Gamma\left(\frac{1}{3}\right)}$$

*Abramovitz and Stegun (1970), p. 446.

Here, $\bar{F}_m$ denotes the mth function of the sequence

$$\bar{F}_m(p) = \frac{1}{p+1} + \frac{(-p)^{m-1/3}}{p+1} + \frac{(-p)^{m-2/3}}{p+1}, \; m \geq 0, \quad (18)$$

and $\bar{N}(p)$ denotes the power series

$$\bar{N}(p) = \frac{1}{d_1} \sum_{m=1}^{\infty} t_m(-\eta) \sum_{i=1}^{\infty} (-p)^{m-i} + \sum_{m=1}^{m} \alpha_m \eta^{3m} p^{m-1}. \quad (19)$$

The key steps leading from Eq. 16 to Eq. 17 are given in Appendix B. While each of the functions $\bar{F}_m(p)$, $m \geq 0$ has a simple pole at $p = -1$ and a branch point at $p = 0$, $\bar{N}(p)$ represents a holomorphic function of p, because both series in expression 19 converge for all p, $0 \leq |p| < \infty$. The convergence of these series can be established by the ratio test given in Appendix A.

Substituting now $\bar{F}(p, \eta)$ in expression 15 by expression 17 changes the inversion formula into:

$$F(\xi,\eta) = \frac{1}{d_1 2\pi i} \int_w e^{\xi p} \sum_{m=0}^{\infty} t_m \bar{F}_m dp - \frac{1}{2\pi i} \int_w e^{\xi p} \bar{N} dp. \quad (20)$$

Because the first and second terms in this expression are integrals of a multi- and single-valued function, respectively, their evaluation can be simplified by adjusting the form of the contour w as follows.

We require that radius r be larger than 1 and that straight lines CD and EF approach the negative real axis to an infinitesimal distance from their respective sides. Figure 1b shows the contour w changed in this way. Consider now the integral over w of a single-valued function whose poles are all contained within the circle ED. The integrals along FE and DC will cancel each other because integration runs in opposite directions, and in the limit of zero distance between these paths, their integrands represent the same function. The integral along the almost closed circle ED will differ from that over the full circle EDE by the value of the integral over the arc DE. However, the integral over DE of any analytic function is zero, as the integrand is bounded there, and the length of the integration path is reduced to zero. Therefore, the integral over w of a single-valued function whose poles are within the circle ED equals $2\pi i$ times the sum of the corresponding residues.

This allows immediate integration of all single-valued functions in expression 20. Since $\bar{N}(p)$ has no poles, the second integral vanishes, and by substituting $\bar{F}_m$ from Eq. 18 into the first one we get:

$$F(\xi,\eta) = \frac{e^{-\xi}}{d_1} \sum_{0}^{\infty} t_m(-\eta) + S^{(1)} + S^{(2)}, \quad (21)$$

where $S^{(1)}$ and $S^{(2)}$ denote the integrals of the two multivalued functions:

$$S^{(k)} = \frac{1}{d_1 2\pi i} \int_w \frac{e^{\xi p}}{p+1} (-p)^{-k/3} \sum_{m=0}^{\infty} t_m(-\eta) \times (-p)^m dp \quad (k = 1, 2). \quad (22)$$

We integrate this series term by term. To show that the conditions for interchange of integration and summation are satisfied, we again consider separately the contributions to the integral of the arc ED and of the straight paths FE and DC in Figure 1b.

The function $e^{\xi p}(-p)^{-k/3}/(p+1)$ is bounded and continuous everywhere on w, and the power series $\Sigma t_m(-p)^m$ has an infinite radius of convergence (Appendix A); therefore, it also converges uniformly on any fixed interval. This is sufficient to reverse the order of integration and summation over the finite interval ED, but not over the infinite intervals FE and DC. The additional condition, which the improper integral along the path $FE + DC$ must satisfy, is given by the following theorem (Bromwich, 1949, theorem B, pp. 499–500):

Theorem (Bromwich, 1949). For any series $\Sigma f_n(z)$ that converges uniformly in any fixed interval $a \leq z \leq b$ with arbitrary b, and any function $\phi(z)$ which is continuous for all finite values of z, the equation

$$\int_a^{\infty} \phi(z) \Sigma f_n(z) dz = \sum \int_a^{\infty} \phi(z) f_n(z) dz$$

holds, provided that either the integral $\int_a^{\infty} |\phi(z)| \Sigma |f_n(z)| dz$ or the series $\Sigma \int_a^{\infty} |\phi(z) f_n(z)| dz$ converges.

When in Eq. 22 the integration is performed along the path $FE + DC$ only, a real integral between the limits of r and ∞ is obtained and the above theorem applies immediately. In this integral, the function $e^{-\xi \rho}(-\rho)^{-k/3}/(\rho - 1)$ and the series $\Sigma_0^{\infty} t_m(-\eta)(-\rho)^m$ correspond to the function $\phi(z)$ and the series $\Sigma f_n(z)$ of the theorem, respectively. Therefore, according to the theorem, the condition for interchange of summation and integration in our problem is the convergence of the series $\Sigma_0^{\infty} |t_m| A_m$, where

$$A_m = \int_r^{\infty} \frac{e^{-\xi \rho}}{\rho - 1} \rho^{m-k/3} d\rho. \quad (23)$$

We now show that this condition is satisfied.

Note first that the integral A_m converges to a positive number for $\xi > 0$ and $m \geq 0$. Next, let $q = r/(r-1)$ and note that the inequality $0 < \rho^{m-k/3}/(\rho - 1) \leq q\rho^{m-k/3-1}$ holds for $1 < r \leq \rho < \infty$ and $m \geq 0$. If we define an auxiliary integral B_m as:

$$B_m = \int_r^{\infty} e^{-\xi \rho} \rho^{m-k/3-1} d\rho = \xi^{k/3-m} \Gamma \times (m - k/3, \xi r), \; \xi > 0 \; (m \geq 1) \quad (24)$$

we also have the inequality $0 < A_m < qB_m$ for $m \geq 0$. For ξ larger than zero, $\Gamma(m - k/3)$ bounds $\Gamma(m - k/3, \xi r)$ from above. Therefore, by defining $C_m = \xi^{k/3-m}\Gamma(m - k/3)$, we obtain one more inequality: $B_m < C_m$ for $m \geq 1$. Considering now the series $\Sigma_1^{\infty} |t_m| C_m$, we find that it converges for all ξ larger than zero (Appendix A). Convergence of the series $\Sigma_0^{\infty} |t_m| A_m$ then follows from convergence of the series $\Sigma_1^{\infty} |t_m| C_m$, inequalities $0 < A_m < qB_m < qC_m$, $m \geq 1$, and convergence of the integral A_0.

Thus, conditions for reversing the order of integration and summation in expression 22 are satisfied over the entire contour w. We then express $S^{(2)}$ and $S^{(1)}$ as series with integral terms and Eq. 21 becomes:

$$F(\xi,\eta)=\frac{1}{d_1}\sum_{m=0}^{\infty} t_m(-\eta)[e^{-\xi}+I_m^{(1)}(\xi)+I_m^{(2)}(\xi)] \quad (25)$$

where

$$I_m^{(k)}(\xi)=\frac{1}{2\pi i}\int_w \frac{e^{\xi p}}{p+1}(-p)^{m-k/3}dp, \quad k=1,2. \quad (26)$$

Existence of the integral $I_m^{(k)}$ follows from that of the integral A_m for all m, and convergence of the series (Eq. 25) is ensured by the theorem (because convergence of $\Sigma_0^\infty |t_m| A_m$ suffices for convergence of $\Sigma_0^\infty t_m I_m^{(k)}$). Expression 25, therefore, represents a new form of the solution. However, we go one step further and show that integrals $I_m^{(k)}$ can be expressed in terms of the function $\gamma^*(\alpha,z)$, called Tricomi's gamma function (Tricomi, 1950; Abramovitz and Stegun, 1970, pp. 260, 262). Specifically, we define the function $v(\alpha,z)$ as:

$$v(\alpha,z)=e^z z^\alpha \gamma^*(\alpha,z) \quad (27)$$

and show that the equality

$$I_m^{(k)}(\xi)=v(k/3-m,-\xi)$$
$$=e^{-\xi}(-\xi)^{k/3-m}\gamma^*(k/3-m,-\xi) \quad \text{for } \xi>0 \quad (28)$$

holds for all $m, m\geq 0$.

For this, we need the recursion property of the function $\gamma^*(\alpha, z)$ (Tricomi, 1950, Eq. 14; Abramovitz and Stegun, 1970, p. 262). In terms of function v, this recursion reads:

$$v(\alpha,z)=v(\alpha-1,z)-\frac{z^{\alpha-1}}{\Gamma(\alpha)}, \ \alpha>0. \quad (29)$$

The term $z^{\alpha-1}/\Gamma(\alpha)$ is a function of α and z, which can be represented by the following integral along the contour w (Doetsch, 1950, pp. 160–163):

$$\frac{1}{2\pi i}\int_w e^{pz}p^{-\alpha}dp=\begin{cases}0 & \text{for } \alpha=0,\ -1,\ -2,\ \ldots \\ \dfrac{z^{\alpha-1}}{\Gamma(\alpha)} & \text{otherwise.}\end{cases} \quad (30)$$

This formula holds for $z>0$, and for $z=1$ it reduces to the well-known Hankel integral form of the complete gamma function. We now use formulas 29 and 30 to prove equality (Eq. 28) by mathematical induction.

Let $m=0$. Then,

$$I_0^{(k)}=\frac{1}{2\pi i}\int_w \frac{e^{\xi p}}{p+1}(-p)^{-k/3}dp=\frac{1}{2\pi i}\int_{Br}\frac{e^{\xi p}}{p+1}(-p)^{-k/3}dp.$$

The second equality follows because the integral satisfies Jordan's lemma: it vanishes over the arcs BC + FA in Figure 1a. Then, $I_0^{(k)}=e^{-\xi}\gamma(k/3,\ -\xi)/\Gamma(k/3)$, as the inverse of the transform $(-p)^{-k/3}/(p+1)$, which was already obtained as the second and third term of the surface concentration function $F_0(\xi)$, (Eq. 11). For $\alpha>0$, $v(\alpha,z)$ can be written as $e^z\gamma(\alpha,z)/\Gamma(\alpha)$ so that $I_0^{(k)} = v(k/3,-\xi)$, and equality (Eq. 28) holds for $m=0$.

Let $m=n$, $n\geq 0$ and assume $I_n^{(k)}=v(k/3-n,-\xi)$. Then for $I_{n+1}^{(k)}$ we write

$$I_{n+1}^{(k)}=\frac{1}{2\pi i}\int_w e^{\xi p}\frac{(-p-1+1)(-p)^{n-k/3}}{p+1}dp$$
$$=-\frac{1}{2\pi i}\int_w e^{\xi p}(-p)^{n-k/3}dp+\frac{1}{2\pi i}\int_w e^{\xi p}\frac{(-p)^{n-k/3}}{p+1}dp$$
$$=\frac{(-\xi)^{k/3-n-1}}{\Gamma(k/3-n)}+v(k/3-n,-\xi). \quad (31)$$

The last equality follows by expressing the first integral according to Eq. 30 and by recognizing the second integral as $I_n^{(k)}$, which was assumed identical to $v(k/3-n,-\xi)$. Applying recursion (Eq. 29) to the last expression, we find $I_{n+1}^{(k)}=v[k/3-(n+1),-\xi]$, or that equality (Eq. 28) for $m=n$ implies the same for $m=n+1$, $n\geq 0$. The equality, therefore, holds for any m, $m\geq 0$.

Substituting for the integrals $I_m^{(k)}$ in expression 25 according to equality 28, we obtain the final form of the series solution:

$$F(\xi,\eta)=\frac{1}{d_1}\sum_{m=0}^{\infty} t_m(-\eta)F_m(\xi) \quad (32)$$

where

$$F_m(\xi)=e^{-\xi}\left[1+(-\xi)^{1/3-m}\gamma^*\left(\frac{1}{3}-m,-\xi\right)\right.$$
$$\left.+(-\xi)^{2/3-m}\gamma^*\left(\frac{2}{3}-m,-\xi\right)\right]$$
$$\times t_m(-\eta)=d_1\alpha_m(-\eta)^{3m}-d_2\beta_m(-\eta)^{3m+1}. \quad (33)$$

The functions $F_m(\xi)$ and $t_m(-\eta)$ are defined for $0<\xi<\infty$ and $0\leq\eta<\infty$, respectively, and the series (Eq. 32) converges for all ξ and η in this domain.

Properties of the series solution

The series solution (Eq. 32) has some convenient properties, important in engineering applications, which derive from the properties of the functional sequence $\{F_m\}$. We show them now.

Expression 33 defines the functional sequence $\{F_m\}$. We take only the real value of $(-\xi)^{k/3-m}$. As $\gamma^*(\alpha,z)$ is an entire function and real-valued for all real α and z, F_m is also real and defined for all nonzero ξ. At $\xi=0$, only F_0 is defined, while functions F_m for m larger than zero are all singular. When $\alpha>0$, function $\gamma^*(\alpha,z)$ can be represented also as $z^{-\alpha}\gamma(\alpha,z)/\Gamma(\alpha)$, so that for $m=0$, expression 33 reduces to expression 11. Thus, as already implied by the notation, the surface concentration function F_0 is the first element of the functional sequence (Eq. 33) and the only one that can be represented also in terms of incomplete gamma functions, $\gamma(\alpha,z)$. In this sense, expression 33 defines the functional sequence $\{F_m\}$ as a generalization of function F_0.

An explicit relationship between F_0 and F_m for $m\geq 1$ follows by applying the recursion (Eq. 29) m times to F_m:

$$F_m(\xi) = F_0(\xi) + \sum_{i=1}^{m} g_i(\xi) \tag{34}$$

where

$$g_i(\xi) = \frac{\sqrt{3}}{2\pi}\left[\frac{\Gamma\left(i-\frac{1}{3}\right)}{\xi^{i-1/3}} - \frac{\Gamma\left(i-\frac{2}{3}\right)}{\xi^{i-2/3}}\right]. \tag{35}$$

Expressing now functions F_m in series (Eq. 32) by this formula, we get a new form for $F(\xi, \eta)$

$$d_1 F(\xi,\eta) = Ai(-\eta)F_0(\xi) + \sum_{m=1}^{\infty} t_m(-\eta) \sum_{i=1}^{m} g_i(\xi), \tag{36}$$

which is more convenient for computation, since it calls for only one evaluation of the special functions Ai and F_0 and for summation of an infinite series whose terms are obtainable by algebraic operations. Computation of F_0 will be addressed later.

The sequence $\{F_m\}$ introduces an essential singularity into the series (Eq. 32), and the solution $F(\xi, \eta)$ is not defined for $\xi = 0$. However, it satisfies the boundary condition at that point, which means that the limit of F as ξ tends to zero is equal to unity, while $F(0, \eta)$ does not exist. Interestingly, the boundary condition as η tends to infinity (Eq. 2c) is satisfied by series (Eq. 32), while neither any one of the functions $t_m(-\eta)/d_1$ nor the series, $Ai(-\eta)/d_1 = \Sigma_0^\infty t_m(-\eta)/d_1$, satisfies that condition. The properties of the functional sequence $\{F_m(\xi)\}$ and its interaction with the sequence $\{t_m(\eta)\}$ are discussed in Appendix C. It shows that the series form of $F(\xi, \eta)$ (Eq. 32) satisfies the boundary conditions in η.

We also note the derivative properties of the sequence $\{F_m\}$. By using the reflection property of the complete gamma function (Abramovitz and Stegun, 1970, p. 256), expression 35 can be shown to result from:

$$g_i(\xi) = (-1)^i \frac{d^i}{d\xi^i}\left[\frac{\xi^{2/3}}{\Gamma\left(\frac{5}{3}\right)} - \frac{\xi^{1/3}}{\Gamma\left(\frac{4}{3}\right)}\right]. \tag{37}$$

From the derivative property of γ^* (Tricomi, 1950, Eq. 16; Abramovitz and Stegun, 1970, p. 262), we obtain the derivative rule for functions F_m:

$$\frac{d^i F_m(\xi)}{d\xi^i} = (-1)^i F_{m+i}(\xi). \tag{38}$$

Applications

We consider now the engineering use of our solution, i.e. the calculation of the mass transfer coefficient and the rate of numerical convergence of functions F_0 and F. We also develop simple approximate formulas for surface concentration and local and average mass transfer coefficients.

Mass transfer coefficient

We define the local mass transfer coefficient $k(\xi)$ as the ratio of flux into the solid surface at a position ξ and the largest concentration difference occurring in the dimensional form of the problem (here $C_0 - C_e$). Because of the form of the boundary condition at $y = 0$ (Eq. 2b), the so-defined local mass transfer coefficient is proportional to surface concentration:

$$\frac{k(\xi)}{k_r} = \frac{Sh(\xi)}{D} = F_0(\xi). \tag{39}$$

Here, k_r denotes the rate constant of the surface reaction, and $Sh(\xi)$ is the local Sherwood number defined analogously to the Damköhler number, $k(\xi)$ taking the place of k_r.

The average mass transfer coefficient over a distance ξ, defined as the usual integral mean of the local one, is:

$$k_a(\xi) = \frac{1}{\xi}\int_0^\xi k(z)dz = \frac{k_r}{\xi}\int_0^\xi F_0(z)dz.$$

This integral can be computed easily by making use of the properties of the functional sequence $\{F_m\}$. With $m = 1$ and $i = 1$, Eq. 34 gives $F_0 = F_1 - g_1$, and by setting $m = 0$ and $i = 1$ in Eqs. 37 and 38, we obtain F_1 and g_1, respectively, in derivative form. Integration of $F_0 = F_1 - g_1$ then gives

$$\frac{k_a(\xi)}{k_r} = \frac{Sh_a(\xi)}{D} = \frac{1 - F_0(\xi)}{\xi} + \frac{\xi^{-1/3}}{\Gamma\left(\frac{5}{3}\right)} - \frac{\xi^{-2/3}}{\Gamma\left(\frac{4}{3}\right)}, \tag{40}$$

where $Sh_a(\xi)$ is the Sherwood number based on the average mass transfer coefficient $k_a(\xi)$.

Computation of the surface concentration

Equation 11 gives the surface concentration in terms of the function $\gamma(\alpha, z)$ with $z < 0$. Although this function is a standard item of commercial libraries of mathematical software, it is often unavailable for negative values of the second argument. For this reason, we show next how F_0 can be calculated for any value of ξ.

By replacing the function γ^* in expression 33 with $m = 0$ by its Taylor series, one obtains a series for F_0 which converges fast for small values of ξ. In fact, two such series exist, corresponding to the Taylor expansions of $\gamma^*(\alpha, z)$ and $e^z\gamma^*(\alpha, z)$ (Tricomi, 1950, Eq. 14; Abramovitz and Stegun, 1970, p. 262):

$$F_0(\xi) = e^{-\xi} + e^{-\xi}\sum_{n=0}^{\infty}\frac{1}{n!} \times \left[\frac{\xi^{n+2/3}}{\Gamma\left(\frac{2}{3}\right)\left(n+\frac{2}{3}\right)} - \frac{\xi^{n+1/3}}{\Gamma\left(\frac{1}{3}\right)\left(n+\frac{1}{3}\right)}\right] \tag{41}$$

and

$$F_0(\xi) = e^{-\xi} + \sum_{n=0}^{\infty}\left[\frac{(-\xi)^{n+2/3}}{\Gamma\left(n+1+\frac{2}{3}\right)} + \frac{(-\xi)^{n+1/3}}{\Gamma\left(n+1+\frac{1}{3}\right)}\right]. \tag{42}$$

The terms of the series in expressions 41 and 42 are similar in magnitude to those of the Taylor expansions of e^{ξ} and $e^{-\xi}$, respectively; therefore, the rate of convergence of series (Eqs. 41 and 42) will be similar to the convergence rate of the latter two. For example, with $\xi = 0.1$, 1, 10, 100 and 1,000, the index of the term of the series in expression 41, which falls below 10^{-8} of the current partial sum, is 5, 11, 32, 159, and 1,171. The terms in expression 42 alternate in sign, and the absolute value of the truncation error is smaller than the absolute value of the first term rejected.

For large values of ξ, the series forms (Eqs. 41 and 42) converge too slowly to be of use. However, the function F_0 has an asymptotic expansion by which it can be approximated very accurately for large values of ξ. We derive it next.

Expressing F_0 by the recursion relation (Eq. 34) we obtain:

$$F_0(\xi) = F_m(\xi) - \sum_{i=1}^{m} g_i(\xi).$$

For any fixed value of ξ, $|F_m(\xi)|$ passes through a minimum with respect to m. The higher the value of ξ, the smaller the magnitude of this minimum, approaching zero as ξ tends to infinity. Therefore, for all large enough ξ, the value of $|F_m(\xi)|$ at the minimum will be smaller than any chosen error tolerance. If by m^* we denote the lowest value of m that satisfies such a criterion, the surface concentration $F_0(\xi)$ will be approximated by the finite sum $-\Sigma_1^{m^*} g_i(\xi)$, with an absolute error smaller than or equal to $|F_{m^*}(\xi)|$. The value of m^* will depend on both the value of ξ and the way in which the error tolerance is defined. We choose the following error criterion:

$$|F_m(\xi)| < 10^{-E} F_0(\xi) \quad \text{for } m = m_E^*, \tag{43}$$

which defines the number m_E^*, such that the neglected term $|F_{m_E^*}|$ does not exceed the fraction 10^{-E} of F_0. The formula which approximates F_0 with this accuracy is then:

$$F_0(\xi) \sim -\sum_{i=1}^{m_E^*} g_i(\xi). \tag{44}$$

For any value of E, m_E^* will be a different function of ξ, defined only for large enough ξ. We tabulated $m_E^*(\xi)$ for $E = 8$ and 16 evaluating $F_m(\xi)$ from a series expression analogous to Eq. 41. The following expressions fit these results:

$$m_8^* = \begin{cases} \text{not defined} & \text{for } \xi < 20, \\ \text{Int}[6 + 150/\xi - \ln\ln(\xi)] & \text{for } 20 \le \xi < 6 \times 10^3 \\ 3 & \text{for } \xi \ge 6 \times 10^3, \end{cases} \tag{45}$$

$$m_{16}^* = \begin{cases} \text{not defined} & \text{for } \xi < 36, \\ \text{Int}[31 + \ln\ln(\xi - 34)] & \text{for } 36 \le \xi < 10^4 \\ 5 & \text{for } \xi \ge 10^4 \end{cases} \tag{46}$$

where Int denotes truncation to integer.

In this way, asymptotic formulas can be derived for any value of the error tolerance E. However, the value of m which gives the smallest possible approximation error by formula 44 corresponds to the term of the series $\Sigma_1^{\infty} g_i(\xi)$ with the smallest absolute value. Regardless of the error which it introduces, this value of m can be found approximately for any ξ by solving the equation $g_m(\xi) = g_{m+1}(\xi)$ for m. It is important to note that the series $\Sigma_1^{\infty} g_i(\xi)$ diverges and that it can be used to approximate the function $F_0(\xi)$, only as a finite sum, whose number of terms is to be determined in one of the ways explained above.

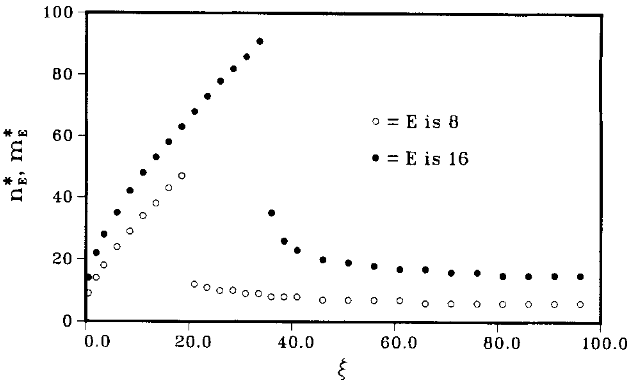

Figure 2. Dependence of the rate of convergence of $F_0(\xi)$ on ξ.

E is the tolerance of error as defined in text. n_E^* is the number of terms of the infinite series in the formula for F_0 for small ξ. m_E^* is the number of terms of the asymptotic expansion.

When the function $m_E^*(\xi)$ is known for a chosen value of E, expressions 41 and 42 need be used only for the values of ξ for which m_E^* is not defined. Figure 2 shows the dependence of the convergence rate of F_0 on the argument ξ when using expression 41 for small ξ and asymptotic formula (Eq. 44) for large ξ. The initial, increasing branch shows the index of the term of the series in expression 41 whose absolute value falls below 10^{-E} of the current partial sum. The decreasing branch shows the number of terms m_E^* of the asymptotic formula (Eq. 44), defined by Eqs. 45 and 46.

Finally, we present simple empirical formulas that approximate surface concentration, local and average mass transfer coefficients with good accuracy for all ξ. We derive these formulas using the Churchill and Usagi method (1972), which consists of matching the asymptotes for large and small values of the argument of the function to be approximated.

For the asymptote of F_0 as ξ tends to zero, from expression 41 we obtain readily:

$$F_0(\xi) \xrightarrow{\xi \to 0} 1.$$

Using the series form (Eq. 41) for F_0 in expression 40 and applying L'Hôpital's rule, the same result follows for the average mass transfer coefficient:

$$\frac{k_a(\xi)}{k_r} \xrightarrow{\xi \to 0} 1.$$

When ξ tends to infinity, according to formula 44, F_0 approaches $-g_1(\xi)$. The asymptote of F_0 is the larger of the two terms of g_1:

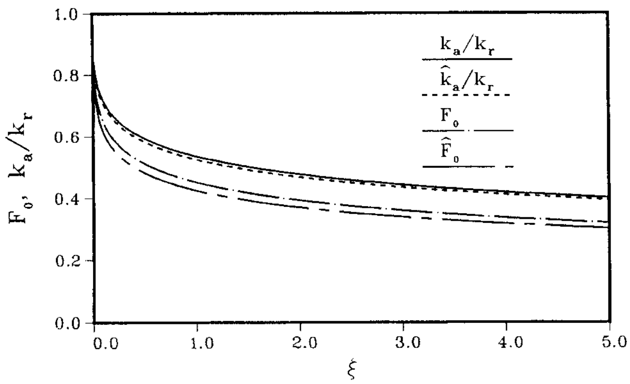

Figure 3. Exact and approximate solutions for surface concentration, local and average mass transfer coefficient.

Lines representing $\tilde{F}_0$ and $\tilde{k}_a/k_r$ are indistinguishable from lines representing F_0 and k_a/k_r, respectively.

$$F_0(\xi) \overset{\xi\to\infty}{\longrightarrow} \frac{\xi^{-1/3}}{\Gamma\left(\frac{2}{3}\right)}. \qquad (47)$$

When used in Eq. 40, this result gives the asymptote of the average mass transfer coefficient at large ξ:

$$\frac{k_a(\xi)}{k_r} \overset{\xi\to 0}{\longrightarrow} \frac{\xi^{-1/3}}{\Gamma\left(\frac{5}{3}\right)}.$$

By matching these asymptotes, according to the Churchill and Usagi method (1972), we obtain the following approximate formulas:

$$\tilde{F}_0(\xi) = \frac{\tilde{k}(\xi)}{k_r} = [1+\Gamma^{n_1}(2/3)\xi^{n_1/3}]^{-1/n_1} = (1+1.394\xi^{0.3649})^{-0.9135}, \qquad (48)$$

$$\frac{\tilde{k}_a(\xi)}{k_r} = [1+\Gamma^{n_2}(5/3)\xi^{n_2/3}]^{-1/n_2} = (1+0.9000\xi^{0.3433})^{-0.9710}, \qquad (49)$$

where tilde denotes approximate values, and $n_1 = 1.0946689$ and $n_2 = 1.0298747$ are the required constants calculated from the analytical solution. Maximum error of these approximations is 1% for $\tilde{F}_0$ and 0.3% for $\tilde{k}_a$. If n_1 and n_2 are both set to 1, very simple approximate formulas are obtained that assume the form of "resistances in series":

$$\frac{1}{k_r\hat{F}_0(\xi)} = \frac{1}{\hat{k}(\xi)} = \frac{1}{k_r} + \frac{1.354\xi^{1/3}}{k_r}, \qquad (50)$$

$$\frac{1}{\hat{k}_a(\xi)} = \frac{1}{k_r} + \frac{0.9027\xi^{1/3}}{k_r}, \qquad (51)$$

where superscript "hat" denotes approximate values at this second level. Maximum errors of these approximations are 6% for $\hat{F}_0$ and 3% for $\hat{k}_a$.

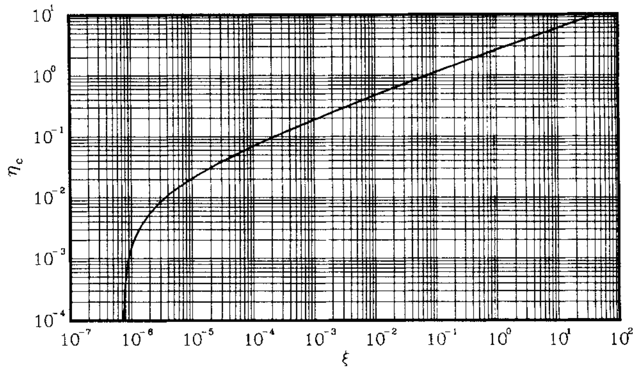

Figure 4. Outer limit of the concentration boundary layer defined as the locus where $F = 0.99$.

The exact and approximate surface concentration and the average mass transfer coefficient are plotted in Figure 3.

Computation of the full solution

To compute the value of F for given arguments ξ and η, we use the second series form (Eq. 36). This series converges quickly for the values of ξ and η, for which F is well below unity, that is, at points within the concentration boundary layer. The outer limit of the concentration boundary layer, defined as the line $\eta_c(\xi)$ on which $F = 0.99$, is shown in Figure 4. Convergence of the series is fast roughly for $\eta < \eta_c$; in contrast to the integral forms (Eqs. 4 and 5), the closer the values of ξ and η are to zero, the faster it becomes. Convergence is slow for $\eta \geq \eta_c$, but that is the region of the $\xi - \eta$ plane, in which the value of F is practically unchanged and is not of great interest.

Figure 5 shows two views of the surface $F(\xi,\eta)$ computed from expression 36 by direct summation of the series.

Examples

When the assumptions noted in the Introduction section hold, $F(\xi,\eta)$ represents an approximation to the solution of heat and mass transfer in many practical problems, such as in chemical reactors with liquid films (wetted catalytic wall columns, experimental reactors, and packed beds in the film regime of flow), developed flow in films and pipes and many cases of boundary layer flow over a solid body on which a

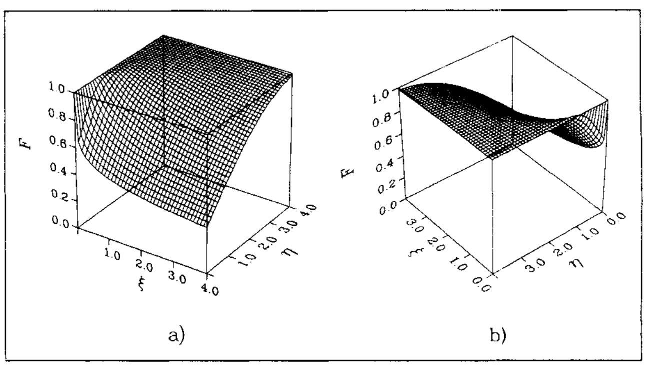

Figure 5. Two views of the surface $F(\xi,\eta)$.

Coordinates of the viewpoint given as (ξ,η,F) are: a) -30, -40, 30; b) -20, 20, 25.

reaction occurs. The dimensional form of the problem (Eqs. 1-2c) for mass transfer in any such application is:

$$qY\frac{\partial C}{\partial X}=\mathfrak{D}\frac{\partial^2 C}{\partial Y^2}, \tag{52}$$

$$X=0,\ 0\leq Y<\infty:\quad C=C_0, \tag{53a}$$

$$0<X<\infty,\ Y=0:\quad \mathfrak{D}\frac{\partial C}{\partial Y}=k_r(C-C_e), \tag{53b}$$

$$0<X<\infty,\ Y\to\infty:\quad C=C_0. \tag{53c}$$

where X and Y denote the distance in the flow direction and the perpendicular direction, respectively, q the gradient of flowwise velocity, assumed constant, and $\mathfrak{D}$ the binary diffusivity of the solute. These equations represent the mass balance of a sparingly soluble substance in a flowing fluid when diffusion in the main flow direction and velocity in the direction perpendicular to it can be neglected. The velocity in the X direction $u(Y)$ is replaced by its linear approximation at $Y=0$.

We consider next the most important cases of fluid flow in which the above problem may serve as a model of heat or mass transfer and examine the conditions of its applicability in terms of the flow parameters. We also define more precisely the limitation to short entrance lengths or high Schmidt numbers, to which the model (Eqs. 52-53c) is usually subject.

Developed pipe and film flow of power law fluids

In a hydrodynamically fully-developed film of a power law fluid, the velocity distribution $u(Y)$ is given by:

$$u=\frac{2n+1}{n+1}\frac{\Gamma}{h}\left[1-\left(\frac{h-Y}{h}\right)^{1+1/n}\right],$$

where n denotes the power law index, Γ the volumetric flow rate per unit width of the solid surface, and h the film thickness. The velocity gradient at the wall is $q=[(2n+1)/n]\Gamma/h$; as velocity in the Y direction is everywhere exactly zero, Eq. 52 applies at short distances from the wall, at which qY approximates $u(Y)$ well and when diffusion in the X direction can be neglected.

In the developed pipe flow of power law fluids, the velocity distribution is:

$$u=\frac{3n+1}{n+1}\frac{Q}{\pi R^2}\left[1-\left(\frac{r}{R}\right)^{1+1/n}\right],$$

where r denotes radial position in the pipe, R the pipe radius, and Q the volumetric flow rate. In this case, by Y we denote the distance $R-r$, measured from the wall, and approximate $u(r)$ again by qY, with $q=[(3n+1)/n]Q/(\pi R^3)$. This approximation will hold close to the wall when $Y\ll R$, which is a condition necessary also to approximate the cylindrical geometry of the pipe by Eq. 52.

The natural length scale in the developed film and pipe flow is the film thickness and the pipe radius, respectively. We take it as the characteristic length in the Y direction and denote it by Y^*. For the direction X, there is no apparent characteristic length and it is convenient to define it as:

$$X^*=\frac{q(Y^*)^3}{\mathfrak{D}}.$$

With this, we formulate the remaining condition of applicability of Eq. 52: the characteristic time of diffusion must be much larger than that of convection in the direction of flow. This condition is equivalent to requiring a large value of the Péclet number, $Pe=(q/\mathfrak{D})^2(Y^*)^4$, and it allows neglecting diffusion in the X direction.

The dimensionless form of the problem (Eqs. 1-2c) then follows by setting $x=X/X^*$, $y=Y/Y^*$, $c=(C-C_e)/(C_o-C_e)$ and by defining the Damköhler number as:

$$D=\frac{k_rY^*}{\mathfrak{D}}. \tag{54}$$

We have restricted the validity of the model to short distances from the wall Y, but in a practical problem this means that the solution c may be accepted only over short distances X. This is so because at large X significant mass transfer takes place farther away from the solid surface, and that is the region in which the linear approximation of the velocity profile does not hold. Whether for a given value of X the solution c may be accepted can be verified by using the solution itself. From Figure 4 we read the outer limit of the concentration boundary layer η_c and find the corresponding actual distance Y. The solution will hold if at that Y the linear velocity profile qY can still be accepted as an approximation of the actual velocity $u(Y)$. In general, linear approximation of velocity will hold better over a longer distance in a power law fluid with a larger exponent n, that is, of a more dilatant character.

Laminar boundary layers

Laminar boundary layers that have a Falkner-Skan solution (Schlichting, 1979) develop between a solid surface and a potential flow whose only velocity component is parallel to the surface and has the form:

$$U(X)=A\left(\frac{X}{X^*}\right)^m. \tag{55}$$

A and m are the parameters describing the outer flow, and X^* is some characteristic length in the direction of the surface, such as length of the solid plate. Then, the quantity

$$\phi=\sqrt{\frac{(m+1)A}{2X^*\nu}}\left(\frac{X}{X^*}\right)^{\frac{m-1}{2}}Y \tag{56}$$

represents the similarity variable for Prandtl's equations of motion within the boundary layer (Schlichting, 1979). The solution is given in terms of f, the dimensionless stream function,

$$f=\sqrt{\frac{m+1}{2AX^*\nu}}\left(\frac{X}{X^*}\right)^{-\frac{m+1}{2}}\psi(X,Y), \quad (57)$$

which depends only on the similarity variable ϕ and satisfies the following ordinary differential equation:

$$f'''+ff''+\frac{2m}{m+1}(1-f'^2)=0,\ f(0)=f'(0)=0,\ \lim_{\phi\to\infty} f'(\phi)=1,$$

where ψ denotes the actual stream function and ν the kinematic viscosity of the fluid. Linear approximation to velocity components in directions X and Y inside the boundary layer follow from this solution as

$$u(X,Y)=q\left(\frac{X}{X^*}\right)^{\frac{3m-1}{2}}Y+\mathcal{O}(Y^2),\ v=0+\mathcal{O}(Y^2), \quad (58)$$

respectively, where q denotes the constant part of the velocity gradient:

$$q=\sqrt{\frac{(m+1)A^3}{2X^*\nu}}f''(0).$$

Tables of values of the dimensionless stream function $f(\phi)$ and its first and second derivative are listed in the reports of Falkner-Skan solutions.

Diffusion in the X direction will be negligible whenever the Péclet number, here defined as $[q(X^*)^2/\mathfrak{D}]^{2/3}$, is much larger than unity. When this condition is satisfied and linear approximations of u and v (Eq. 58) are used, the mass balance equation becomes:

$$q\left(\frac{X}{X^*}\right)^{\frac{3m-1}{2}}Y\frac{\partial C}{\partial X}=\mathfrak{D}\frac{\partial^2 C}{\partial Y^2}.$$

For the characteristic length in the Y direction we use $(\mathfrak{D}X^*/q)^{1/3}$, and to transform the above equation into the form of Eq. 52, we make the change of variables:

$$\chi=\frac{2}{3(1-m)}x^{3(1-m)/2}.$$

Then, after scaling concentration C we obtain the dimensionless problem (Eqs. 1-2c), in which χ takes the place of x. Therefore, solution c with x replaced by χ applies also to mass transfer in laminar boundary layers that have a Falkner-Skan solution with $m<1$.

While the thickness of both momentum and concentration boundary layer grows with X, their ratio will remain approximately equal to $Sc^{0.5}$. Therefore, the above formulation of the mass transfer in boundary layers, sometimes called modified Lévêque's model, is limited to systems with large Schmidt numbers, so that the linear approximations of velocity remains valid. In contrast to film and pipe flow, how good these approximations are will be determined by the value of the Schmidt number, rather than the distance X.

Like Lighthill's model (Lighthill, 1950), this one also assumes a linear profile of the velocity component u close to the surface and uses the new variable χ to remove the dependence of the shear stress at the wall on x. However, Lighthill's model does not require setting the velocity component v to zero, as was done here, and instead of the coordinate y it uses the stream function, ψ (von Mises's coordinates in Schlichting, 1979). For this reason, modified Lévêque's model should not be expected to hold for values of the Schmidt number as low as Lighthill's model ($Sc\approx 0.7$), but this still allows its application to a great many systems of practical importance.

Discussion and Conclusions

The series solution presented here completes a set of solutions of Lévêque's equation for all three types of boundary conditions in terms of different kinds of gamma functions. Let ξ and η be the dimensionless coordinates that reduce the problem to the simplest form for each boundary condition. Then, Lévêque's differential equation reads:

$$\eta\frac{\partial F}{\partial \xi}=\frac{\partial^2 F}{\partial \eta^2},$$

and the boundary conditions and the corresponding solutions assume the forms listed in Table 2.

Expression 59 is the well-known similarity solution of classical Lévêque's problem (Lévêque, 1928). Boundary conditions of the second and the third kind do not admit a similarity variable; however, the corresponding solutions (expressions 60 and 61) are fixed by specifying only two independent variables, whereas fixing the values of the corresponding dimensional problems requires specifying three parameters (the two coordinates and the value of the surface flux in problem 60 and the coordinates and the reaction rate for problem 61).

Solutions of the first two problems in terms of incomplete gamma functions, $\Gamma(\alpha,z)$ or $\gamma(\alpha,z)$, have been known for a long time (Bird et al., 1960; Lévêque, 1928). We have shown the solution of the third problem to be representable in the useful form (Eq. 61) through another one of the gamma functions, Tricomi's gamma function, $\gamma^*(\alpha,z)$. The following integral representation for this function, valid for $z>0$ and all real α, is a side result of our inversion procedure and we believe it to be new:

Table 2. Solutions of Lévêque's Problem for Boundary Conditions of the First, Second and Third Kind*

$F(\xi,0)=0$ $F(0,\eta)=F(\xi,\infty)=1$	$F=\dfrac{\gamma\left(\frac{1}{3},\zeta\right)}{\Gamma\left(\frac{1}{3}\right)}$	(59)
$F_\eta(\xi,0)=1$ $F(0,\eta)=F(\xi,\infty)=0$	$F=(9\xi)^{1/3}\dfrac{e^{-\zeta}-\zeta^{1/3}\Gamma(2/3,\zeta)}{\Gamma\left(\frac{2}{3}\right)}$	(60)
$F_\eta(\xi,0)=dF(\xi,0)$ $F(0,\eta)=F(\xi,\infty)=1$	$F=\dfrac{1}{d_1}\sum_{m=0}^{\infty}t_m(-\eta)F_m(\xi)$	(61)

*$\zeta=\eta^3/(9\xi)$, $d=d_2/d_1$.

$$\frac{1}{2\pi i}\int_w e^{zp}\frac{(-p)^{-\alpha}}{p+1}dp = v(\alpha,-z) = e^{-z}(-z)^{\alpha}\gamma^*(\alpha,-z)$$

For noninteger real α, this follows by the proof of equality 28 given earlier. For the integer values of α, the integrand is single-valued, and by summing the residues, as explained, we obtain simpler results. In summary:

$$v(\alpha,-z) = \begin{cases} (-1)^{\alpha}e^{-z} & \text{for } \alpha = 0,-1,-2,\cdots \\ e^{-z} - \sum_{i=1}^{\alpha-1}\frac{(-z)^i}{i!} & \text{for } \alpha = 1,2,\cdots \\ e^{-z}(-z)^{\alpha}\gamma^*(\alpha,-z) & \text{for noninteger real } \alpha. \end{cases}$$

The results for integer values of α are the simplified forms of the function $v(\alpha, -z)$, which are due to the properties of the function γ^* (Tricomi, 1950).

According to the boundary condition (Eq. 2b), solution (Eq. 59) should represent the limit of solution (Eq. 61) as the Damköhler number tends to infinity. We illustrate this for the local Sherwood number $Sh(\xi)$. We recall first that $Sh(\xi)/D = F_0(\xi)$ (Eq. 39). As $\xi = a^3x = D^3x/d^3$, the limit of $Sh(\xi)/D$ as D tends to infinity is the same as the limit of $F_0(\xi)$ as ξ tends to infinity for a fixed value of x. Therefore, Eq. 47 applies readily to give:

$$\frac{Sh(\xi)}{D} \xrightarrow{D\to\infty} \frac{\xi^{-1/3}}{\Gamma\left(\frac{2}{3}\right)} = \frac{d}{\Gamma\left(\frac{2}{3}\right)}\frac{x^{-1/3}}{D}.$$

After evaluating the last expression, this result reduces to:

$$\lim_{D\to\infty} Sh(\xi) = 3^{1/3}\frac{x^{-1/3}}{\Gamma\left(\frac{1}{3}\right)}.$$

The same result is obtained from Eq. 59, because in that problem ξ and η equal x and y, respectively, and $Sh(x)$ is the gradient $\partial F/\partial y$ at $y=0$.

We showed the series solution (Eq. 61) to have properties useful for algebraic calculations and to converge rapidly inside the concentration boundary layer. Explicit expressions for surface concentration and mass transfer coefficients and mathematical properties which bear on their computation were presented. This establishes the series solution (Eq. 61) as both practical and mathematically well-described, rather than as a merely formal one. These were the objectives of our study.

The method by which we arrived at our solution is the classical procedure of contour integration with the difference that a series form of the Laplace transform was used and integration was performed term by term. In this sense, our solution starts with the formal inversion integral (Eq. 15) and evaluates it by breaking up the integrand into a series. It is exactly this procedure that gives the series solution its useful properties which the formal integral forms (Eqs. 4 and 5) lack.

Although inversion by term-by-term integration requires only the standard theory of complex variables and some classical analysis, it is not a popular technique in chemical engineering. It should be said, however, that even the standard texts mention this method only as a way of obtaining asymptotic solutions (e.g., MacLachlan, 1953; Van der Pol and Bremmer, 1950; Doetsch, 1950). In addition to presenting a new solution form of Lévêque's problem with the boundary condition of the third kind, this work shows the utility of term by term integration as a method of inversion of the Laplace transform.

Acknowledgment

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Notation

a = constant d_2D/d_1
A = constant in the expression for U
Ai = Airy function, Table 1
Bi = "bairy" function
c = dimensionless concentration, $(C-C_e)/(C_0-C_e)$, as a function of x and y
C = actual concentration
d = d_2/d_1
d_1 = value of Ai at 0, Table 1
d_2 = value of $-Ai'$ at 0, Table 1
D = Damköhler number, $k_rY^*/\mathfrak{D}$
E = criterion of accuracy, Eq. 43
$\mathfrak{D}$ = binary diffusivity of the solute
f = dimensionless stream function
F = dimensionless concentration as a function of ξ and η
F_m = functions defined by Eq. 33
F_0 = surface concentration function, Eq. 11
g_i = function defined by Eq. 35
h = thickness of a liquid film
I = function defined by Eq. 26
k = local mass transfer coefficient at the solid surface
k_r = rate constant of the surface reaction
m = constant in the expression for U
m_E^* = number of terms required in asymptotic form for F_0, Figure 2
$M(\cdot,\cdot,\cdot)$ = Kummer's function
N = function defined by Eq. 19
n = power law index
n_E^* = number of terms required in exact series form of F_0, Figure 2
n_1 = constant in formula 48
n_2 = constant in formula 49
p = argument of the Laplace transform taken with respect to ξ, s/a^3
Pe = Péclet number
q = gradient of the velocity u in the Y direction
Q = volumetric flow rate
r = radial position
R = radius of the pipe
s = argument of Laplace transform taken with respect to x
Sh = Sherwood number, $kY/\mathfrak{D}$
t = $s^{1/3}y$
t_m = terms of Taylor series for Ai, Table 1
u = actual velocity in the X direction
U = velocity in the outer flow, Eq. 55
v = actual velocity in the Y direction
$v(\alpha, z)$ = $e^zz^{\alpha}\gamma^*(\alpha, z)$
x = dimensionless coordinate X
X = actual coordinate parallel to the solid surface
X^* = characteristic length in the X direction
y = dimensionless coordinate Y
Y = actual coordinate perpendicular to the solid surface

Y^* = characteristic length in the Y direction
z = dummy variable

Greek letters

α, β = dummy variables
α_m, β_m = coefficients in the power expansion of Airy function, Table 1
$\gamma(\cdot,\cdot)$ = incomplete gamma function
$\gamma^*(\cdot,\cdot)$ = Tricomi's gamma function
Γ = flow rate per unit width of wetted surface
$\Gamma(\cdot)$ = complete gamma function
$\Gamma(\cdot,\cdot)$ = complementary incomplete gamma function
ζ = similarity variable, $\eta^3/(9\xi)$
η = scaled variable y, ay
ν = kinematic viscosity
ξ = scaled variable x, a^3x
χ = $2x^{3(1-m)/2}/[3(1-m)]$
ψ = stream function

Subscripts

a = integral average
c = at the outer limit of boundary layer
e = at equilibrium
o = at $X=0$

Miscellaneous

$\bar{}$ = Laplace transform
$'$ = first derivative
$\tilde{}$ = at the first level of approximation
$\hat{}$ = at the second level of approximation

Literature Cited

Abramovitz, M., and I. A. Stegun, eds., *Handbook of Mathematical Functions*, Dover Publications, New York (1970).

Apelblat, A., "Mass Transfer with Chemical Reaction of the First Order: Analytical Solutions," *Chem. Eng. J.*, **19**, 19 (1980).

Bird, R. B., W. E. Stewart, and E. N. Lightfoot, *Transport Phenomena*, p. 363, Wiley, New York (1960).

Bromwich, T. J. I'A., "An Introduction to the Theory of Infinite Series," 2nd ed., McMillan, London (1949).

Chambré, P. L., "On Chemical Surface Reactions in Hydrodynamic Flows," *Appl. Sci. Res.*, Hague, **A6**, 97 (1956).

Churchill, S. W., and R. Usagi, "A General Expression for the Correlation of Mass Transfer Rates and Other Phenomena," *AIChE J.*, **18**, 1121 (1972).

Doetsch, G., *Einführung in Theorie und Andwendung der Laplace-Transformation*, Birkhäuser Verlag, Basel (1950).

Erdélyi, A., ed., *Tables of Integral Transforms*, Vol. 1, McGraw-Hill, New York (1954).

Den Hartog, H. J., and W. J. Beek, "Local Mass Transfer with Chemical Reaction: II. Heterogeneous Reactions," *Appl. Sci. Res.*, Hague, **A19**, 338 (1968).

Friedman, M. H., "Transport Through a Growing Boundary Layer to a Permeable Wall," *AIChE J.*, **22**, 407 (1976).

Ghez, R., "Mass Transport and Surface Reactions in Lévêque's Approximation," *Int. J. Heat Mass Transfer*, **21**, 745 (1978).

LePage, W. R., *Complex Variables and the Laplace Transform for Engineers*, Dover Publications, New York (1961).

Lighthill, M. J., "Contributions to the Theory of Heat Transfer Through a Laminar Boundary Layer," *Proc. Roy. Soc. London*, **A202**, p. 359 (1950).

Lévêque, M. A., "Les lois de la transmission de chaleur par convection," *Ann. Mines*, **13**, 201 (1928).

MacLachlan, N. W., *Complex Variable Theory and Transformation Calculus*, 2nd ed., Cambridge University Press (1950).

Van der Pol, B., and H. Bremmer, *Operational Calculus Based on the Two-Sided Laplace Integral*, Cambridge University Press (1950).

Tricomi, F. G., "Sulla funzione gamma incompleta," *Ann. Mat. Pura Appl.: IV*, Vol. 31, p. 263 (1950).

Appendix A: Convergence of the Series of the Form $\Sigma t_m a_m$

We use d'Alembert's ratio test to establish the convergence of any series of this form. For convergence, it is necessary to show that the limit of $\Sigma |t_{m+1}a_{m+1}/t_m a_m|$ as m tends to infinity is smaller than 1.

We first simplify the term $\lim_{m\to\infty} |t_{m+1}/t_m|$, which appears in all series of this form. By factoring $\alpha_m(-\eta)^{3m}$ from t_m (Table 1) we obtain:

$$|t_m a_m| = \frac{3^m \Gamma\left(m+\frac{1}{3}\right)}{\Gamma\left(\frac{1}{3}\right)(3m)!}\eta^{3m} \times \left| d_1 + d_2\eta\Gamma\left(m+\frac{2}{3}\right) \Big/ \Gamma\left(m+\frac{4}{3}\right) \right| |a_m|,$$

and therefore,

$$\lim_{m\to\infty}\frac{|t_{m+1}a_{m+1}|}{|t_m a_m|} = \lim_{m\to\infty}\frac{\eta^3/3}{(3m+3)(3m+2)} \times \left|\frac{d_1+d_2\eta\Gamma(m+5/3)/\Gamma(m+7/3)}{d_1+d_2\eta\Gamma(m+2/3)/\Gamma(m+4/3)}\right| \frac{|a_{m+1}|}{|a_m|}$$
$$= \frac{\eta^3}{3}\lim_{m\to\infty}\frac{|a_{m+1}/a_m|}{(3m+3)(3m+2)} \quad \text{for } 0\le\eta<\infty. \qquad (A1)$$

Next, we consider the convergence of different series of this form, corresponding to different forms of the term a_m:

a) $\Sigma\tau_m(-p)^m$. In this case, $a_m=(-p)^m$, and from Eq. A1

$$\lim_{m\to\infty}\frac{|t_{m+1}(-p)^{m+1}|}{|t_m(-p)^m|} = \frac{\eta^3|p|}{3}\lim_{m\to\infty}\frac{1}{(3m+3)(3m+2)}=0,$$

for $0\le\eta<\infty$ and $0\le|p|<\infty$.

b) $\Sigma t_m C_m$. In this case, $a_m=C_m=\xi^{k/3-m}\Gamma(m-k/3)$, and Eq. A1 gives

$$\lim_{m\to\infty}\frac{|t_{m+1}C_{m+1}|}{|t_m C_m|} = \frac{\eta^3}{3\xi}\lim_{m\to\infty}\frac{m-k/3}{(3m+3)(3m+2)}=0,$$

for $0\le\eta<\infty$ and $0<\xi<\infty$.

c) $F(\xi,\eta)$. We represent F by the form (Eq. 36) and test the convergence of the series $\Sigma_1^\infty t_m\Sigma_1^m g_i$. We have

$$\frac{|a_{m+1}|}{|a_m|} = \frac{|\Sigma_1^{m+1} g_i(\xi)|}{|\Sigma_1^m g_i(\xi)|} \xrightarrow{m\to\infty} \frac{m-\frac{1}{3}}{\xi}$$

and

$$\lim_{m\to\infty}\frac{|t_{m+1}a_{m+1}|}{|t_m a_m|} = \frac{\eta^3}{3\xi}\lim_{m\to\infty}\frac{m-\frac{1}{3}}{(3m+3)(3m+2)}=0,$$

for $0 \leq \eta < \infty$ and $0 < \xi < \infty$.

Appendix B: Series form of $\overline{F}(p,\eta)$

The function $\overline{F}_0(p)$, defined by Eq. 10, satisfies the following two identities:

$$\frac{1}{p(1+p^{1/3})} \equiv \frac{1}{p} - \overline{F}_0(p) \equiv p^{-1/3}\overline{F}_0(p). \qquad \text{(B1)}$$

Replacing Ai in expression 16 by its Taylor series (Table 1), we obtain:

$$\overline{F}(p,\eta) = \frac{1}{p} - \frac{1}{d_1}\frac{1}{p(1+p^{1/3})} \times \left(d_1 \sum_{m=0}^{\infty} \alpha_m p^m \eta^{3m} - d_2 \sum_{m=0}^{\infty} \beta_m p^{m+1/3} \eta^{3m+1} \right).$$

Expressing now the coefficient in front of the first and the second series according to the first and the second identity in expression B1, respectively, gives:

$$\overline{F}(p,\eta) = \frac{1}{p} - \sum_{m=0}^{\infty} \alpha_m p^{m-1}\eta^{3m} + \overline{F}_0 \sum_{m=0}^{\infty} \alpha_m p^m \eta^{3m} + \frac{d_2}{d_1}\overline{F}_0 \sum_{m=0}^{\infty} \beta_m p^m \eta^{3m+1}$$

$$= -\sum_{m=1}^{\infty} \alpha_m p^{m-1}\eta^{3m} + \sum_{m=0}^{\infty} \eta^{3m} b_m \left[\frac{p^m}{p+1} - \frac{p^{m-1/3}}{p+1} + \frac{p^{m-2/3}}{p+1} \right], \qquad \text{(B2)}$$

where $b_m = \alpha_m + d_2\beta_m\eta/d_1$. Next, we express the term $p^m/(1+p)$ in terms of positive powers of p using the theorem about transforming derivatives:

$$\frac{p^m}{p+1} = \mathcal{L}\left(\frac{d^m e^{-\xi}}{d\xi^m}\right) + \sum_{i=1}^{m} p^{m-i}(-1)^{i-1} = \frac{(-1)^m}{p+1} - (-1)^m \sum_{i=1}^{m} (-p)^{m-i}, \; m \geq 1.$$

Substituting this result in Eq. B2, and setting $-p^{m-1/3} = (-1)^m(-p)^{m-1/3}$ and $p^{m-2/3} = (-1)^m(-p)^{m-2/3}$ allows factoring the term $(-1)^m$. Equation 17 then follows by recognizing that $(-1)^m b_m \eta^{3m} = t_m(-\eta)/d_1$.

Appendix C: Boundary Conditions in η

When written in terms of η, the boundary condition (Eq. 2b) takes the form $F_\eta(\xi,0) = dF_0$. It is satisfied, because $t'_0 = d_2$ and $t'_m(0) = 0$ for $m > 0$, so that $F_\eta(\xi,0) = \Sigma t'_m(0)F_m/d_1 = dF_0$.

The other boundary condition in y in terms of η reads $\lim_{\eta\to\infty} F = 1$. To show that it holds takes some manipulation. We start by taking the partial derivative of F with respect to ξ:

$$F_\xi = -\frac{1}{d_1}\sum_{m=0}^{\infty} t_m F_{m+1} = -\frac{1}{d_1}\sum_{m=0}^{\infty} t_m (F_m + g_{m+1}).$$

The first equality follows from the derivative property of the functions F_m, Eq. 38 and the second one from their recursion property (cf. Eq. 34). We use the above equation because it expresses F in terms of a single, rather than double infinite series:

$$F_\xi + F = -\frac{1}{d_1}\sum_{m=0}^{\infty} t_m(-\eta) g_{m+1}(\xi).$$

Next, expanding the term $t_m g_{m+1}$ produces four terms that give rise to four infinite series, representing the following four functions of ζ:

$$F_\xi + F = -\frac{\xi^{-2/3}}{\Gamma\left(\frac{1}{3}\right)} e^{-\zeta} - \frac{\xi^{-1/3}\zeta^{1/3}}{\Gamma\left(\frac{1}{3}\right)} \frac{\Gamma\left(\frac{2}{3}\right)}{\Gamma\left(\frac{4}{3}\right)} M\left(\frac{2}{3}, \frac{4}{3}, -\zeta\right) + \frac{\xi^{-1/3}}{\Gamma\left(\frac{1}{3}\right)} M\left(\frac{1}{3}, \frac{2}{3}, -\zeta\right) + \frac{\gamma\left(\frac{1}{3}, \zeta\right)}{\Gamma\left(\frac{1}{3}\right)}. \qquad \text{(C1)}$$

Here M denotes the Kummer's function (Abramovitz and Stegun, 1972, p. 504). We consider next the limit of each term as η, or equivalently, ζ, tends to infinity. Setting $F_\xi = F_{\eta\eta}/\eta$ according to the differential equation, instead of $\lim_{\eta\to\infty} F_\xi$, we consider the limit $\lim_{\eta\to\infty} F_{\eta\eta}/\eta$ and find it zero, because the series $d_1 F_{\eta\eta} = \Sigma t''_m F_m$ converges for all η, including when η tends to infinity (proof is analogous to case c in Appendix A). Next, we replace $M(\alpha,\beta,z)$ by its asymptotic form, $\Gamma(\beta)z^\alpha[1+\mathcal{O}(z^{-1})]\Gamma(\alpha)$, corresponding to large negative z (Abramovitz and Stegun, 1972, p. 504). Then, taking the limit as η tends to infinity of Eq. C1 with these substitutions, we get:

$$\lim_{\eta\to\infty} \frac{F_{\eta\eta}}{\eta} + \lim_{\eta\to\infty} F = -\frac{\xi^{-2/3}}{\Gamma\left(\frac{1}{3}\right)} \lim_{\zeta\to\infty} e^{-\zeta} - \frac{\xi^{-1/3}}{\Gamma\left(\frac{1}{3}\right)} \lim_{\zeta\to\infty} \zeta^{1/3}\zeta^{-2/3}[1+\mathcal{O}(\zeta^{-1})] + \frac{\xi^{-1/3}}{\Gamma\left(\frac{1}{3}\right)} \lim_{\zeta\to\infty} \zeta^{-1/3}[1+\mathcal{O}(\zeta^{-1})] + \lim_{\zeta\to\infty} \frac{\gamma\left(\frac{1}{3}, \zeta\right)}{\Gamma\left(\frac{1}{3}\right)},$$

which reduces to the desired result:

$$\lim_{\eta\to\infty} F = 1.$$

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