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A method to dynamically estimate the diffusion boundary layer from local velocity conditions in laminar flows

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Abstract

The differential equation for dilute species transport next to a planar interface within the hydrodynamic boundary layer is transformed into a differential equation for the diffusion boundary layer. This differential equation contains two coefficients, which depend explicitly on the concentration profile. We show that these coefficients can be taken as identical constants, in a number of limiting cases. Using these constants, we show that this equation reproduces very well the temporal and spatial profile of the diffusion boundary layer determined from numerical simulations in some more complex intermediate cases. The final differential equation depends only on the diffusion coefficient and on local velocity and velocity gradients next to the interface, and not explicitly on concentration. Therefore this equation can be used to estimate the mass transfer coefficient from the local velocity profile when conditions are not fixed in space or time, and especially in transient computational fluid dynamics calculations. It can also be used to estimate new correlations for the mass transfer coefficient, in cases where the spatial velocity profile at the interface is known.

Keywords: Mass transfer; Fluid mechanics; Simulation; Laminar flow; Boundary layer

1. Introduction

Computational fluid dynamics has become an essential tool for the study of any system involving heat or mass transfer, particularly for the optimisation of engineering devices [1]. Heat and mass are exchanged at the boundary between two fluid streams through the so-called stagnant boundary layer, where the ultimate cause of transport is diffusion [2]. Then transfer is univocally determined by the condition of equilibrium of the fluxes at the interface.

$$\phi = D_1 \frac{\partial c_1}{\partial z}\bigg|_{z=0} = D_2 \frac{\partial c_2}{\partial z}\bigg|_{z=0}, \tag{1}$$

where D_i indicates the diffusion coefficient in phase i, c_i the concentration in phase i, and z the co-ordinate perpendicular to the interface between the phases, $z = 0$ denoting the interface itself. In many practical cases

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Nomenclature

x, y, z	orthogonal axes (m)
u, v, w	velocity field along x, y, and z (m/s)
u_0	fluid velocity at the interface $z = 0$ (m/s)
ϕ	mass flux at the interface (kg/m^2 s)
D_i	species diffusion coefficient in phase i (m^2/s)
c_i	species concentration field in phase i (kg/m^3)
c_0	concentration field at position $z = 0$ (kg/m^3)
c_∞	concentration field at position $z = \infty$ (kg/m^3)
$\tilde{c}$	reduced concentration field
k	mass transfer coefficient (m/s)
k_i	mass transfer coefficient in phase $i = 1, 2$ (m/s)
δ	boundary layer for mass transport (m)
δ_i	mass transport boundary layer in phase $i = 1, 2$ (m)
Δ_i	distance between the interface and the centre of the first computational cell normal to the interface (m)
Re	Reynolds number
Sc	Schmidt number
Sh	Sherwood number
τ_w	wall shear stress at $z = 0$ (kg/m s^2)
t	time (s)
$\eta = z/\delta$	reduced coordinate normal to the interface
$\Gamma(n)$	complete gamma function
erf(x)	error function

one introduces the so-called mass transfer coefficient, defined so that

$$\phi = k(\bar{c}_2 - \bar{c}_1), \tag{2}$$

where $\bar{c}_i$ indicates now the average value of the concentration in phase i, and we have omitted any equilibrium partition coefficient for simplicity.

Whenever the computational mesh in a CFD model is finer than the size of this diffusion boundary layer, one can directly use the condition of equilibrium of the flux (1) to determine the flux between the two phases. However when the computational mesh is larger than the diffusion boundary layer, one cannot resolve the concentration gradient at the interface, and hence use of a transfer coefficient becomes compulsory. The size of this boundary layer depends essentially on the magnitude of the diffusion coefficient: a few millimetres or more for mass transfer in gas phase, where $D \sim 10^{-5}$ m^2/s; and a few microns for mass transfer in the liquid phase, where $D \sim 10^{-9}$ m^2/s. Clearly most cases involving mass transfer in a liquid require the introduction of a mass transfer coefficient.

The estimation of this mass transfer coefficient constitutes a difficult and recurrent problem in applications of CFD [3,4]. Very generally, correlations derived from known cases are introduced in the calculation. These correlations are derived by solving explicitly for the species concentration c, for given conditions of diffusion and advection. There are many existing correlations applying to a wide range of physical flow situations, listed in different books and reviews [2]. In most cases different flow situations require different forms of correlations, as do different system geometry. Furthermore these correlations describe the average situation in the system, and not the local conditions. Finally they mostly apply to steady-state cases, unsteady cases being much more difficult to treat [5–7]. Therefore the use of such correlations breaks down when treating a system where flow conditions vary as a function of time.

It would be most convenient in these cases to define the mass transfer coefficient from local conditions of the flow in the computational cells bordering the interface. Unfortunately, to the best of our knowledge no such correlation exists. Since this mass transfer coefficient does not represent a real physical quantity, there exists no elementary equation governing its behaviour. However the definition of k shows that it only depends on the value of concentration and its derivative at the interface, that is, on local quantities, so that nothing prevents k to be defined based on local conditions. Limiting ourselves to the case of laminar flows close to a planar interface, we show here that it is possible to construct a local differential equation governing the evolution of k, reproducing known average correlations in all limiting cases. We argue that this differential equation has a broader application and can be used to estimate k in those cases, where no correlations exist, as an efficient way to interpolate existing results.

Rather than working with k or its equivalent Sherwood number Sh, we chose to use as our primary variable the size of boundary layer δ, defined as $\delta = D/k$. Indeed, small boundary layers such as encountered in well-mixed systems result in mass transfer coefficients tending to infinity, which is quite impractical in computations.

In the next section we construct the differential equation for δ based on a weak solution of the specie equation. We determine the coefficients of this differential equation from the analytical solution in a number of limiting cases. In Section 3 we show that this equation also reproduces correlations in some intermediate cases for which they are known from previous studies, as well as in some specific numerical examples: this suggests its more general applicability. Finally we conclude in Section 4.

2. Boundary layer equation

2.1. Derivation

Consider a laminar flow next to a planar interface in two dimensions, as depicted in Fig. 1. In the dilute limit, a passive scalar quantity is advected by the flow and diffuses according to

$$\frac{\partial c}{\partial t}+\frac{\partial}{\partial x}(uc)+\frac{\partial}{\partial z}(wc)=D\frac{\partial^2 c}{\partial z^2}+D\frac{\partial^2 c}{\partial x^2}, \tag{3}$$

where c is the concentration in scalar, u is the velocity in the plane of the interface, w is the velocity perpendicular to the interface, and D the specie diffusion coefficient. Supposing further that axial diffusion is much smaller than normal diffusion, that is

$$\frac{\partial^2 c}{\partial x^2}\ll\frac{\partial^2 c}{\partial z^2}, \tag{4}$$

we have

$$\frac{\partial c}{\partial t}+\frac{\partial}{\partial x}(uc)+\frac{\partial}{\partial z}(wc)=D\frac{\partial^2 c}{\partial z^2}. \tag{5}$$

Rather than the actual concentration profile, we can use a dimensionless concentration profile

$$\tilde{c}=\frac{c-c_\infty}{c_0-c_\infty}, \tag{6}$$

where c_0 and c_∞ indicate the concentration profiles at position $z = 0$ (at the interface) and z = infinity (deep into the medium). This concentration profile is valid for $c_0 \neq c_\infty$ and $\frac{\mathrm{D}}{\mathrm{D}t}c_0=\frac{\mathrm{D}}{\mathrm{D}t}c_\infty=0$. For $c_0 = c_\infty$ there is no mass transfer at the interface so that $\delta = \infty$. Using this dimensionless variable we have

$$\frac{\partial \tilde{c}}{\partial t}+\frac{\partial}{\partial x}(u\tilde{c})+\frac{\partial}{\partial z}(w\tilde{c})=D\frac{\partial^2 \tilde{c}}{\partial z^2}, \tag{7}$$

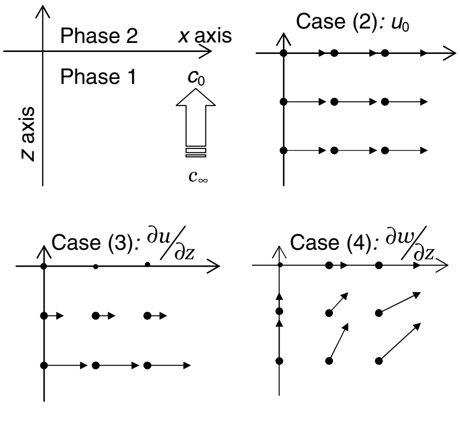

Fig. 1. Local flow conditions next to the interface. Vectors indicate the velocity field close to the interface. The case number refers to the cases defined in Section 2.1.

with boundary conditions

$$\tilde{c}(z=0)=1, \tag{8}$$

$$\tilde{c}(z=\infty)=0. \tag{9}$$

The boundary layer δ is defined as

$$\frac{1}{\delta}=\left|\frac{\partial \tilde{c}}{\partial z}\right|_{z=0} \tag{10}$$

Note that some definitions set the boundary layer from a fixed value of $c/(c_0 - c_\infty)$. Use of the above definition in Eq. (10), however, rigorously defines the mass transfer coefficient at the interface as the flux of specie through the interface. A weak solution of Eq. (7) can be obtained by integrating over the boundary layer:

$$\int_{z=0}^{z=\delta(x,t)}\frac{\partial \tilde{c}}{\partial t}\mathrm{d}z+\int_{z=0}^{z=\delta(x,t)}\frac{\partial}{\partial x}(u\tilde{c})\mathrm{d}z+\int_{z=0}^{z=\delta(x,t)}\frac{\partial}{\partial z}(w\tilde{c})\mathrm{d}z$$
$$=\int_{z=0}^{z=\delta(x,t)}D\frac{\partial^2\tilde{c}}{\partial z^2}\mathrm{d}z. \tag{11}$$

Use of Leibniz rule for the two left integrals and direct integration for the two rightmost integrals give

$$\frac{\partial}{\partial t}\int_{z=0}^{z=\delta(x,t)}\tilde{c}\,\mathrm{d}z-\frac{\partial\delta}{\partial t}\tilde{c}|_{z=\delta}+\frac{\partial}{\partial x}\int_{z=0}^{z=\delta(x,t)}(u\tilde{c})\,\mathrm{d}z$$
$$-\frac{\partial\delta}{\partial x}(u\tilde{c})_{z=\delta}+w\tilde{c}|_{z=\delta}-w\tilde{c}|_{z=0}$$
$$=D\left(\left.\frac{\partial\tilde{c}}{\partial z}\right|_{z=\delta}-\left.\frac{\partial\tilde{c}}{\partial z}\right|_{z=0}\right). \tag{12}$$

We limit ourselves to a class of problem where mass transfer across the interface is much faster than any change of the velocity profile at the interface. Considering that $w(0) = 0$ and use of the variable $\eta = z/\delta$ gives

$$\frac{\partial}{\partial t}\left[\delta\int_{\eta=0}^{\eta=1}\tilde{c}\,\mathrm{d}\eta\right]-\frac{\partial\delta}{\partial t}\tilde{c}_{\eta=1}+\frac{\partial}{\partial x}\left[\delta\int_{\eta=0}^{\eta=1}(u\tilde{c})\,\mathrm{d}\eta\right]$$
$$-\frac{\partial\delta}{\partial x}(u\tilde{c})_{\eta=1}+w\tilde{c}|_{z=\delta}=\frac{D}{\delta}\left(1+\left.\frac{\partial\tilde{c}}{\partial\eta}\right|_{\eta=1}\right). \tag{13}$$

We expect the reduced variable $c(\eta)$ to be independent of time and distance, as this dependence is entirely taken up by the diffusion boundary layer δ from which η is defined. On the other hand, integrals involving velocity will not be independent of distance. Hence

$$\frac{\partial\delta}{\partial t}\left[\int_{\eta=0}^{\eta=1}\tilde{c}\,\mathrm{d}\eta-\tilde{c}_{\eta=1}\right]$$
$$+\frac{\partial\delta}{\partial x}\left[\int_{\eta=0}^{\eta=1}(u\tilde{c})\,\mathrm{d}\eta-(u\tilde{c})_{\eta=1}\right]$$
$$+\delta\frac{\partial}{\partial x}\left[\int_{\eta=0}^{\eta=1}(u\tilde{c})\,\mathrm{d}\eta\right]+w\tilde{c}|_{z=\delta}$$
$$=\frac{D}{\delta}\left(1+\left.\frac{\partial\tilde{c}}{\partial\eta}\right|_{\eta=1}\right). \tag{14}$$

In the third term, only the velocity u should depend directly on x, which allows us to write

$$\begin{aligned}&\frac{\partial\delta}{\partial t}\left[\int_{\eta=0}^{\eta=1}\tilde{c}\,\mathrm{d}\eta-\tilde{c}_{\eta=1}\right]\\&\quad+\frac{\partial\delta}{\partial x}\left[\int_{\eta=0}^{\eta=1}(u\tilde{c})\,\mathrm{d}\eta-(u\tilde{c})_{\eta=1}\right]\\&\quad+\delta\int_{\eta=0}^{\eta=1}\frac{\partial u}{\partial x}\tilde{c}\,\mathrm{d}\eta+w\tilde{c}|_{z=\delta}\\&\quad=\frac{D}{\delta}\left(1+\frac{\partial\tilde{c}}{\partial\eta}\bigg|_{\eta=1}\right).\end{aligned}\tag{15}$$

Since, from the continuity equation, $\frac{\partial u}{\partial x}=-\frac{\partial w}{\partial z}$, we can write

$$\begin{aligned}&\frac{\partial\delta}{\partial t}\left[\int_{\eta=0}^{\eta=1}\tilde{c}\,\mathrm{d}\eta-\tilde{c}_{\eta=1}\right]\\&\quad+\frac{\partial\delta}{\partial x}\left[\int_{\eta=0}^{\eta=1}(u\tilde{c})\,\mathrm{d}|\eta-(u\tilde{c})_{\eta=1}\right]\\&\quad-\delta\int_{\eta=0}^{\eta=1}\frac{\partial w}{\partial z}\tilde{c}\,\mathrm{d}\eta+w\tilde{c}|_{z=\delta}=\frac{D}{\delta}\left(1+\frac{\partial\tilde{c}}{\partial\eta}\bigg|_{\eta=1}\right).\end{aligned}\tag{16}$$

This equation is general, for the dilute solution. We can make further progress by making some assumptions on the actual velocity profile within the hydrodynamic boundary layer. As indicated in introduction, our aim is to derive a master equation for δ, for use in cases where we can describe the hydrodynamic boundary layer, but not the diffusion boundary layer. Accordingly, we assume that the flow is locally linear, so that it is described by the following parameters:

- horizontal velocity at the surface u_0;
- gradient of horizontal velocity $\frac{\partial u}{\partial z}$ (shear);
- gradient of vertical velocity $\frac{\partial w}{\partial z}$ (strain).

The vertical velocity at δ can then be approximated as

$$w|_{z=\delta}\sim\frac{\partial w}{\partial z}\delta.\tag{17}$$

Furthermore, $\frac{\partial w}{\partial z}$ should not depend on η within the bounds of the integral, so that we can write

$$\begin{aligned}&\frac{\partial\delta}{\partial t}\left[\int_{\eta=0}^{\eta=1}\tilde{c}\,\mathrm{d}\eta-\tilde{c}_{\eta=1}\right]\\&\quad+\frac{\partial\delta}{\partial x}\left[\int_{\eta=0}^{\eta=1}(u\tilde{c})\,\mathrm{d}\eta-(u\tilde{c})_{\eta=1}\right]\\&\quad+\frac{\partial w}{\partial z}\delta\left(\tilde{c}|_{\eta=1}-\int_{\eta=0}^{\eta=1}\tilde{c}\,\mathrm{d}\eta\right)\\&\quad=\frac{D}{\delta}\left(1+\frac{\partial\tilde{c}}{\partial\eta}\bigg|_{\eta=1}\right),\end{aligned}\tag{18}$$

which can also be expressed in function of δ^2:

$$\begin{aligned}&\frac{\partial\delta^2}{\partial t}+\frac{\partial\delta^2}{\partial x}\frac{\left[\int_{\eta=0}^{\eta=1}(u\tilde{c})\,\mathrm{d}\eta-(u\tilde{c})_{\eta=1}\right]}{\left[\int_{\eta=0}^{\eta=1}\tilde{c}\,\mathrm{d}\eta-\tilde{c}_{\eta=1}\right]}\\&\quad=2\frac{\partial w}{\partial z}\delta^2+D\frac{2\left(1+\frac{\partial\tilde{c}}{\partial\eta}|_{\eta=1}\right)}{\left[\int_{\eta=0}^{\eta=1}\tilde{c}\,\mathrm{d}\eta-\tilde{c}_{\eta=1}\right]}.\end{aligned}\tag{19}$$

We further suppose that $u(z)$ can be written as

$$u(x,t,z)=u_0(x,t)+\frac{\partial u}{\partial z}(x,t)z.\tag{20}$$

Then

$$\begin{aligned}&\frac{\partial\delta^2}{\partial t}+\frac{\partial\delta^2}{\partial x}\left[u_0+\frac{\partial u}{\partial z}\delta\frac{\int_{\eta=0}^{\eta=1}\tilde{c}\eta\,\mathrm{d}\eta-\tilde{c}_{\eta=1}}{\int_{\eta=0}^{\eta=1}\tilde{c}\,\mathrm{d}\eta-\tilde{c}_{\eta=1}}\right]\\&\quad=2\frac{\partial w}{\partial z}\delta^2+D\frac{2\left(1+\frac{\partial\tilde{c}}{\partial\eta}\Big|_{\eta=1}\right)}{\left[\int_{\eta=0}^{\eta=1}\tilde{c}\,\mathrm{d}\eta-\tilde{c}_{\eta=1}\right]},\end{aligned}\tag{21}$$

or, put in a simpler form

$$\frac{\partial\delta^2}{\partial t}+\frac{\partial\delta^2}{\partial x}\left[u_0+B\frac{\partial u}{\partial z}\delta\right]=2\frac{\partial w}{\partial z}\delta^2+AD,\tag{22}$$

where

$$B=\frac{\int_{\eta=0}^{\eta=1}\tilde{c}\eta\,\mathrm{d}\eta-\tilde{c}_{\eta=1}}{\int_{\eta=0}^{\eta=1}\tilde{c}\,\mathrm{d}\eta-\tilde{c}_{\eta=1}},\quad A=\frac{2\left(1+\frac{\partial\tilde{c}}{\partial\eta}\Big|_{\eta=1}\right)}{\int_{\eta=0}^{\eta=1}\tilde{c}\,\mathrm{d}\eta-\tilde{c}_{\eta=1}}.\tag{23}$$

Any further progress must make use of an explicit formulation of the concentration profile. Clearly, in general the coefficients A and B will be dependent on the actual problem, as they involve explicitly the concentration profile. We will now look at several examples in limiting cases, and show that in these cases we can use constant coefficients, to form a single equation valid in all these limiting cases. These limiting cases are the simplest ones, as they each involve a minimum number of terms. However they are not the only ones, where the exact solution is known: we show in the next section that the general equation found from the simplest limiting cases also works in less simple situations. The different cases considered here are depicted in Fig. 1 (∂_t indicates the unsteady term):

1. $\partial_t\neq 0$, $u_0=0$, $\frac{\partial u}{\partial z}=0$, $\frac{\partial w}{\partial z}=0$: unsteady diffusion without convection;
2. $\partial_t=0$, $u_0\neq 0$, $\frac{\partial u}{\partial z}=0$, $\frac{\partial w}{\partial z}=0$: steady-state flowing surface without shear not strain;
3. $\partial_t\neq 0$, $u_0=0$, $\frac{\partial u}{\partial z}\neq 0$, $\frac{\partial w}{\partial z}=0$: steady-state flow with a constant shear;
4. $\partial_t\neq 0$, $u_0=0$, $\frac{\partial u}{\partial z}=0$, $\frac{\partial w}{\partial z}\neq 0$: steady-state flow with constant strain. Note that in this case, the existence of a velocity gradient along z for w leads necessarily to a non-zero surface velocity u_0 for an incompressible flow.

To derive the differential equation we assume that the velocity profile is known and fixed in space and time. This implicitly supposes that the diffusion boundary layer resides completely within the hydrodynamic boundary layer. Furthermore, unless stated otherwise, we always assume that all velocities are constant along the surface.

2.2. *Unsteady diffusion*

The simplest correlation to be found is for a purely diffusive system, without convection. The differential equation for concentration in one dimension reads

$$\frac{\partial \tilde{c}}{\partial t} = D\frac{\partial^2 \tilde{c}}{\partial z^2}. \tag{24}$$

In this well-known case, the concentration profile is an error function [2]:

$$\tilde{c}(z,t) = 1 - \operatorname{erf}\left(\frac{z}{\sqrt{4Dt}}\right), \tag{25}$$

and boundary layer increases with time as

$$\delta = \sqrt{\pi D t}. \tag{26}$$

The coefficient A can be calculated by two equivalent ways: By transforming Eq. (26) into a differential equation governing δ^2, we find

$$\frac{\partial \delta^2}{\partial t} = \pi D, \tag{27}$$

which shows that the coefficient A in this limiting case should be $A = \pi$. Alternatively, we can directly evaluate the integrals of Eq. (23), which results in the same value.

2.3. *Steady-state flowing surface without shear nor strain*

In the case of a uniform flow at a constant velocity u_0 next to the surface, we have

$$u_0\frac{\partial \tilde{c}}{\partial x} = D\frac{\partial^2 \tilde{c}}{\partial z^2}. \tag{28}$$

This case is clearly the same as the previous one, from which we get concentration profile and boundary layer. By the same transformation, we have

$$u_0\frac{\partial \delta^2}{\partial x} = \pi D, \tag{29}$$

which corresponds to the reduction of Eq. (22) to this case, again with the coefficient $A = \pi$.

2.4. *Flow with a constant shear and no surface velocity*

We now have the following equation:

$$\frac{\partial u}{\partial z} z\frac{\partial \tilde{c}}{\partial x} = D\frac{\partial^2 \tilde{c}}{\partial z^2}. \tag{30}$$

This is known as the Lévêque problem [2,8]. The concentration profile can be written as

$$\tilde{c}(z) = \frac{\Gamma\left(\frac{1}{3}, \frac{\partial u}{\partial z}\frac{z^3}{9Dx}\right)}{\Gamma\left(\frac{1}{3}\right)}, \tag{31}$$

where $\Gamma(n)$ is the complete gamma function. The boundary layer then is

$$\delta = \left(\frac{Dx}{3}\right)^{1/3}\left(\frac{\partial u}{\partial z}\right)^{-1/3}\Gamma\left(\frac{1}{3}\right). \tag{32}$$

From this it follows that the boundary layer should follow the equation:

$$B\frac{\partial u}{\partial z}\delta\frac{\partial \delta^2}{\partial x} = AD, \tag{33}$$

where $A = \pi$, $B = \frac{9\pi}{2\Gamma^3(1/3)} = 0.735$ and the initial condition $\delta(x = 0) = 0$.

2.5. *Constant strain without shear*

Let us first assume in this case that the diffusion is negligible. The governing equation for c reads

$$u_0\frac{\partial \tilde{c}}{\partial x} + \frac{\partial w}{\partial z} z\frac{\partial \tilde{c}}{\partial z} = 0. \tag{34}$$

Since $\frac{\partial w}{\partial z} \neq 0$, u_0 cannot be constant along the surface for an incompressible flow, so we shall not make this assumption. The solution of Eq. (34) along z is a simple exponential profile:

$$\tilde{c}(x,z) = 1 - \exp \alpha z, \tag{35}$$

where α can depend on x. Replacing in Eq. (34) shows that α needs to be the solution of:

$$u_0\frac{\partial \alpha}{\partial x} + \frac{\partial w}{\partial z}\alpha = 0, \tag{36}$$

from which follows, since $\delta = 1/\alpha$:

$$u_0\frac{\partial \delta^2}{\partial x} = 2\frac{\partial w}{\partial z}\delta^2, \tag{37}$$

without any restriction on the initial conditions. This is indeed the restriction of Eq. (22) to this particular case.

When including the diffusion term in this profile, we now have

$$u_0\frac{\partial \tilde{c}}{\partial x} + \frac{\partial w}{\partial z} z\frac{\partial \tilde{c}}{\partial z} = D\frac{\partial^2 \tilde{c}}{\partial z^2}, \tag{38}$$

If u_0 does not depend on z, the resulting profile along z is an error function

$$\tilde{c}(x,z) = \operatorname{erf}[\alpha(x)z] \tag{39}$$

Inserting in Eq. (38) gives the resulting equation for α

$$u_0\frac{\partial \alpha}{\partial x} + \frac{\partial w}{\partial z}\alpha = -2D\alpha^3, \tag{40}$$

From the profile we see that the boundary layer is $\delta = \sqrt{\pi}/2\alpha$, and hence δ follows the differential equation

$$u_0 \frac{\partial \delta^2}{\partial x} = 2\frac{\partial w}{\partial z}\delta^2 + \pi D, \tag{41}$$

which is indeed the reduction of Eq. (22) in this particular case, with again the coefficient $A = \pi$.

2.6. Total differential equation

In the preceding subsections, we have shown that the c-dependent coefficients of Eq. (22) are actually identical constants in several limiting cases of interests. From there we argue that taking these as constant in intermediate cases will allow us to find the solution for the diffusion boundary layer in these intermediate cases. Hence we write the general equation as

$$\frac{\partial \delta^2}{\partial t} + \left(u_0 + 0.735\frac{\partial u}{\partial z}\delta\right)\frac{\partial \delta^2}{\partial x} = \pi D + 2\frac{\partial w}{\partial z}\delta^2. \tag{42}$$

This 2D equation can of course be straightforwardly extended to 3D by adding the term $\frac{\partial \delta^2}{\partial y}$.

3. Validations

3.1. Analytical validations

By construction, Eq. (42) allows reproducing limiting cases of the boundary layer in some determined flow situations. From there we argue that it will also be valid to estimate the boundary layer size in other cases, that are either intermediate or combinations of the limiting cases defined above. In this section we show that it is indeed so, in some intermediate cases where the solution is known.

3.1.1. Developing flow above a flat plate

Eq. (29) was derived in the particular case of a flow with a constant velocity gradient, that does not depend on x. However this is not a general case. In particular, the shear rate for a developing flow above a flat plate with a constant velocity u_∞ at infinity is [2]:

$$\tau_w = \mu\left.\frac{\partial u}{\partial z}\right|_{z=0} = 0.332\left(\frac{\rho u_\infty x}{\mu}\right)^{-1/2}\frac{1}{2}\rho u_\infty^2. \tag{43}$$

At the interface the horizontal velocity u_0 is zero, so that both w and $\frac{\partial w}{\partial z}$ are equal to zero. Hence Eq. (22) reduces to

$$0.735\frac{\partial u}{\partial z}\delta\frac{\partial \delta^2}{\partial x} = \pi D. \tag{44}$$

Introducing the velocity profile given by Eq. (43) into Eq. (42) and solving for δ, with the initial condition $\delta(x = 0) = 0$, gives

$$\delta = \left(\frac{2\pi}{0.244}\right)^{1/3}\left(\frac{\mu}{\rho u_\infty^3}\right)^{1/6} D^{1/3}x^{1/2}. \tag{45}$$

In terms of Sherwood, Reynolds and Schmidt numbers this solution can be written as

$$Sh_x = \frac{x}{\delta} = 0.339 Re^{1/2} Sc^{1/3}. \tag{46}$$

This is indeed the known correlation for this case [2].

3.1.2. Shear flow with a flowing surface

Here we assume again a shear flow but add a surface velocity u_0 which gives the following equation for diffusion in the dilute limit:

$$\left(u_0 + \frac{\partial u}{\partial z}z\right)\frac{\partial \tilde{c}}{\partial x} = D\frac{\partial^2 \tilde{c}}{\partial z^2}. \tag{47}$$

We suppose that the velocities do not depend on x. The solution in this case is given by Beek and Bakker [3], but has no simple analytical form. Using our present treatment, Eq. (42) reduces to

$$\left(u_0 + 0.735\frac{\partial u}{\partial z}\delta\right)\frac{\partial \delta^2}{\partial x} = \pi D, \tag{48}$$

from which we get, with the initial condition $\delta(x = 0) = 0$

$$u_0\delta^2 + \frac{2}{3}B\frac{\partial u}{\partial z}\delta^3 = \pi D x. \tag{49}$$

We can write $\delta = f(x)$ in the limiting cases of large and small δ. For δ large, that is, $\frac{2B}{3u_0}\frac{\partial u}{\partial z}\delta \gg 1$, we have

$$\delta^3 \approx \frac{3}{2}\frac{\pi D x}{B}\left(\frac{\partial u}{\partial z}\right)^{-1} \times \left\{1 + \frac{3}{2}\frac{u_0}{B}\left(\frac{\partial u}{\partial z}\right)^{-1}\left(\frac{2B}{3\pi D x}\frac{\partial u}{\partial z}\right)^{1/3}\right\}^{-1}. \tag{50}$$

In terms of a Taylor expansion for the mass transfer coefficient k, this equation can be rewritten as

$$k \sim 0.539\left(\frac{\partial u}{\partial z}\frac{D^2}{x}\right)^{1/3} + 0.197\left(\frac{D}{x^2}\left(\frac{\partial u}{\partial z}\right)^{-1}\right)^{1/3}, \tag{51}$$

which is indeed the correlation written by Beek and Bakker [3] for this limit. For δ small, that is, $\frac{2B}{3u_0}\frac{\partial u}{\partial z}\delta \ll 1$, then

$$\delta^2 \approx \frac{\pi D x}{u_0}\left\{1 + \frac{2}{3}\frac{B}{u_0}\left(\frac{\partial u}{\partial z}\right)\left(\frac{\pi D x}{u_0}\right)^{-1/2}\right\}^{-1}, \tag{52}$$

that is,

$$k \sim \left(\frac{u_0 D}{\pi x}\right)^{1/2} + 0.246\left(\frac{D}{u_0}\frac{\partial u}{\partial z}\right). \tag{53}$$

Again we find the correlation as obtained by Beek and Bakker [3] for this limiting case.

3.2. Numerical validations

In order to complement the analytical validations presented above, we have performed a number of comparisons between the boundary layer determined by CFD in some intermediate cases, and the predictions of Eq. (42). We would like to stress that these validations are intended to demonstrate the interest of our present treatment, but do not constitute an exhaustive study on its range of applicability, which has yet to be performed. We have constructed a simple 2-dimensional box measuring 2×5 m as sketched in Fig. 2, equipped with a Cartesian computational mesh $m_z \times \mathrm{m}_x$. The $x = 0$ plane has a constant concentration $c = 1$, the bottom $z = 0$ plane has a fixed concentration $c = 0$ with no surface resistance, the plane $x = L_x$ is an outlet with no defined concentration, and the plane $z = L_z$ is adiabatic. Hence we expect the development of a diffusion boundary layer at the bottom $z = 0$ side. To ensure that the mesh captures this diffusion layer, we have used an increasingly fine mesh next to $z = 0$, and a large diffusion coefficient $D = 10^{-3}$ m^2/s. The velocity field is fixed and constant in time, but may vary as a function of x and z in a prescribed way, so as to reproduce conditions expected in the hydrodynamic boundary layer. In all cases we assumed an incompressible flow so that $\partial u/\partial x = -\partial w/\partial z$. All calculations were performed using the STAR code from Computational Dynamics, Ltd. [9]. The boundary layer δ is determined from the simulation as

$$\delta = \frac{c_0 - c_\infty}{(\partial c/\partial z)_{z=0}}. \tag{54}$$

Eq. (42) was integrated numerically using a totally implicit integration scheme, with the boundary condition $\delta = 0$ at $x = 0$.

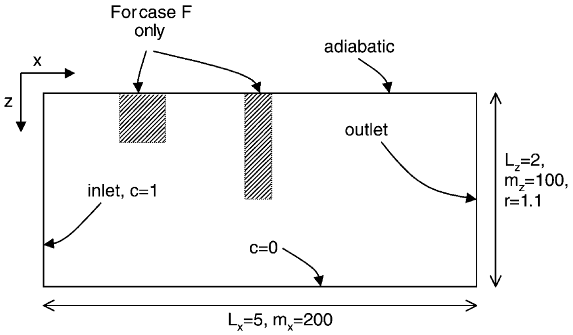

Fig. 2. Sketch of the computational model used for numerical validations. The model includes 200 elements along x and 100 along z, where the density of elements away from the interface $z = 0$ decreases so that two successive elements have a ratio of size equal to 1.1.

3.2.1. Steady-state

Six different cases noted A to F have been considered, and compared to the solution of Eq. (42). The latter was either solved analytically or numerically, depending on the case.

A. $u(x,z) = u_0 + \gamma x$, $w(x,z) = -\gamma z$.
This case corresponds to a flowing surface with a constant strain but no shear. We used $u_0 = 0.1$, $\gamma = 0.1$. The solution in this case is analytical, assuming $\delta(x = 0) = 0$:

$$\delta = \sqrt{\pi D x\left(u_0 + \frac{\gamma}{2}x\right)(u_0 + \gamma x)^{-1}}. \tag{55}$$

B. $u(x,z) = u_0 - \gamma x$, $w(x,z) = \gamma z$.
This case is the same as A, but the velocity gradients point in an opposite direction. In this case we used $u_0 = 0.6$, $\gamma = 0.1$, which ensures that the velocity vectors are always oriented towards $x > 0$. The analytical solution is the same as for case A.

C. $u(x,z) = u_0 + \alpha z + \gamma x$, $w(x,z) = -\gamma z$.
In this case we add a constant shear. The term including $\partial u/\partial z$ is multiplied by δ^3, while the term involving u_0 is only multiplied by δ^2. Since the boundary layer is expected to be small, $\frac{\partial u}{\partial z}$ has to be large compared to u_0 for this velocity gradient to have any influence on the resulting boundary layer: therefore we used here $u_0 = 0.1$, $\gamma = 0.1$, $\alpha = 10.0$.

D. $u(x,z) = u_0 - \beta \cos \pi x$, $w(x,z) = -\beta \pi z \sin \pi x$.
This case is similar to A, except that the surface velocity and the strain depend on x. We used $u_0 = 0.1$, $\beta = 0.05$.

E. $u(x,z) = u_0 + \alpha z - \beta \cos \pi x$, $w(x,z) = -\beta \pi z \sin \pi x$.
This case is similar to *d*, with addition of a constant shear. We used $u_0 = 0.1$, $\beta = 0.05$, $\alpha = 10.0$.

F. This constitutes a 'real-life' test. The system is transformed by adding two vertical wedges on the top surface, as described in Fig. 2. The velocity and velocity gradients are determined by computation on the same grid, with the following conditions: at inlet ($x = 0$), $u = 0.1$ m/s; the upper surface is a no-slip wall, and the bottom surface a slip wall. The liquid is assumed to be water: hence the Schmidt number in this simulation is very low, $Sc \sim 10^{-3}$. Eq. (42) is integrated numerically, using the resulting velocity profile.

Fig. 3 shows an excellent agreement between the computations and integration of Eq. (42). For the simplest cases A–C the agreement is almost exact. For more complex cases, and especially for the 'real-life' case F,

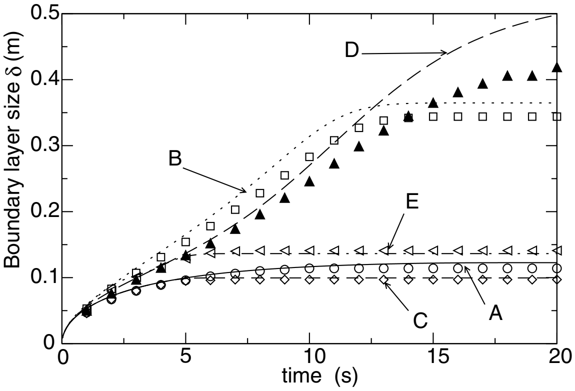

Fig. 3. Boundary layer determined from numerical simulations in the steady-state (points) with the predictions by Eq. (15) (curves). Letters refer to the specific cases described in the text. A: solid line, circles; B: dotted line, squares; C: dashed line, diamond; D: long dashed line, black triangles; E: dot-dashed line, white triangles; F: dot-long dashed line, crosses.

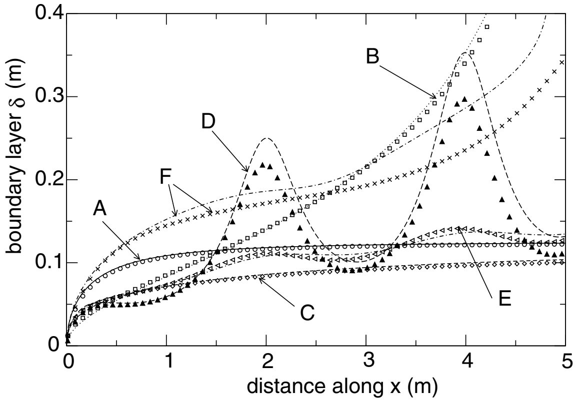

Fig. 4. Boundary layer determined from numerical simulations in transient regime (points) and the predictions of Eq. (15) (curves) at $x = 4$. Letters refer to the specific cases described in the text. A: solid line, circles; B: dotted line, squares; C: dashed line, diamond; D: long dashed line, black triangles; E: dot-dashed line, white triangles.

Eq. (15) predicts correctly both the order of magnitude and the variations of the boundary layer thickness. This is especially remarkable, since in the latter case the magnitude of the diffusion boundary layer is of the same order as or even larger than that of the hydrodynamic boundary layer.

Although this figure only shows cases when the agreement is good, we should note that this is not always the case. In particular, Eq. (42) was derived assuming that the velocity profile can be completely characterised by only three terms, that is, $u_0(x), \frac{\partial u}{\partial z}(x)$, and $\frac{\partial w}{\partial z}(x)$. We have noted that, whenever the variation the vertical velocity can not be described by $\frac{\partial w}{\partial z}$ only over the size of the boundary layer, Eq. (42) gives results that may be qualitatively different from the simulations.

3.2.2. Transient

Transient diffusion was simulated on the same grid as for the steady state, for 20 s with a time-step of 0.1 s. In all cases the velocity profile was fixed in time, so that we only solved for species transport. Eq. (42) was solved numerically. The same five cases A–E presented in the preceding paragraph in steady-state were used for transient validations. Fig. 4 presents the resulting time evolution of the boundary layer size, from simulation (points) and from Eq. (42) (curves), for the specific value $x = 4$. Again we find an excellent agreement between the predictions of simulations and those of Eq. (42).

3.3. Implementation

Eq. (42) can be used within a CFD calculation to estimate mass transfer coefficients, in all cases where the computational mesh is fine enough to resolve the hydrodynamic boundary layer, but too coarse to resolve the diffusion boundary layer. In this case the user should first solve for the momentum equation, then use the corresponding velocity field to estimate δ by integrating Eq. (42) at the interface, and finally solve for the concentration. Although the aim of this article is not to present a complete study utilising this method, we would like to offer some practical suggestions as to its practical implementation. Indeed, the diffusion flux at an interface between phases 1 and 2 is computed using an equation similar, but not identical to, Eq. (2)

$$\phi = k(c_2 - c_1), \tag{56}$$

where the difference comes from the fact that c_1 and c_2 are evaluated at the computational cells neighbouring the interface rather as average over the computational domain. The mass transfer coefficient k can be separated in two contributions, one from each side of the interface

$$\frac{1}{k} = \frac{1}{k_1} + \frac{1}{k_2}. \tag{57}$$

If the computational mesh is smaller than the diffusion boundary layer, then Eq. (1) leads to the following mass transfer coefficient (for example on side 1)

$$k_1 = \frac{D_1}{\Delta_1}, \tag{58}$$

where D_1 is the diffusion coefficient on side 1 and Δ_1 the distance between the centre of the first computational cell and the interface. On the other hand, if the computational mesh is larger than the boundary layer, then by definition of the boundary layer δ_1 the mass transfer coefficient becomes

$$k_1 = \frac{D_1}{\delta_1}, \tag{59}$$

where the boundary layer δ_1 is estimated using Eq. (42). This suggests that the following expression for the mass transfer coefficient should be used in practice

$$k_1 = \frac{D_1}{\max(\Delta_1, \delta_1)}. \tag{60}$$

Eq. (60) clearly shows that large values of the boundary layer, in practice, will not affect the mass transfer at the interface. This is very satisfying, as Eq. (42) is only valid for small δ., while nothing prevents Eq. (42) to result in an infinite boundary layer. In practice, it is therefore necessary to set an upper limit to the increase of δ. While this upper limit does not affect the mass transfer, it might affect the later evolution of δ as a function of time, and therefore is not well defined. However, some preliminary tests performed using either Δ or the model size L as the upper limit on δ did not show any major difference in the general mass transfer.

4. Conclusion

We have written a differential equation governing the behaviour of the diffusion boundary layer size δ for a laminar flow next to a planar interface. This equation presents two coefficients, which are dependent on the actual concentration profile. We show that these coefficients can be taken as identical constant, for a number of relevant limiting cases. When applying the resulting differential equation with constant coefficients to other cases, which are either slightly different or combinations of the cases for which it has been derived, the value of δ from known correlations is reproduced. This equation also reproduces the temporal and spatial dependence of δ computed numerically for a number of different time-independent velocity profiles. Clearly the fact that this equation gives good results in these cases does not impart any general validity, or guaranty it will work in any other cases. However since it allows, by construction, to find all limiting cases of interest, and since intermediate cases are also reproduced, we argue that it provides an accurate and efficient mean to estimate the size of the boundary layer in any intermediate case.

This differential equation is intended primarily to be used in computational fluid dynamics calculations, where it can provide an efficient mean to estimate the mass transfer coefficient at a liquid/liquid or liquid/gas interface from knowledge of the local velocity profile in adjacent cells. It can also be used to construct new correlations $Sh = f(Re, Sc)$ for different physical cases where the flow profile is known. Eq. (30) presents a typical example for such a correlation.

We have limited this study to the mass transfer coefficient next to a planar interface. However this equation should be applicable for other surface geometries, by reinterpreting x and z as local coordinates in the plane of the interface and perpendicular to the interface. It might be also possible to determine a similar equation for the heat transfer coefficient. However our equation has been written for simple flow situations, and makes therefore implicitly use of the fact that the size of diffusion boundary layer is much smaller than the hydrodynamic boundary layer for most liquids, that is, $Sc \gg 1$. We would advise caution whenever the sizes of the boundary layers are not so disparate.

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