Statistical Approximations in Gas–Liquid Mass Transfer

Harry. E. Schulz[1,2], André. L. A. Simões[2] and Johannes G. Janzen[3]

[1] *Nucleus of Thermal Engg. and Fluids, São Carlos School of Engg., University of São Paulo 13566-590, Av. Trabalhador São-carlense 400, São Carlos, S.P., Brazil, heschulz@sc.usp.br*
[2] *Dept. of Hydraulics and Sanitation, São Carlos School of Engg., University of São Paulo 13566-590, Av. Trabalhador São-carlense 400, São Carlos, S.P., Brazil, simoes@sc.usp.br*
[3] *Dept. of Hydraulics and Transport, Federal University Mato Grosso do Sul, Cidade Universitária, Campo Grande-MS 79070-900, Brazil, johannesjanzen@gmail.com*

Abstract. The one-dimensional mass transfer in turbulent flows is considered. The closure problem related to the mean product between concentration and velocity fluctuations is treated by using random square waves. This approximation allows us to represent the statistical variables of turbulent mass transfer as depending on a finite set of basic parameters. The number of equations needed is then limited by the number of basic parameters used. The analysis is applied, in this study, to the interfacial mass transfer at air-water interfaces, generating a closed set of three equations involving three unknown functions. The resulting differential equations are nonlinear. A simplified example is solved.
Key Words: Statistical turbulence, one-dimensional mass transfer, random square waves

1. Introduction

Situations in which physical parameters oscillate randomly are usually difficult to quantify. Turbulence in fluids is an example, in which parameters like velocity and mass concentration oscillate continuously. Statistical equations are often generated for turbulent movement and transport (see, for example, Pope, 2000). It is known that the statistical description of turbulence generates more variables than equations to solve them, a situation known as the "closure problem" of turbulence (Hinze 1959, and Monin and Yaglom 1979, 1981).

Theoretical approximations for statistical profiles of concentration fluctuations below the water surface were presented by Schulz and Schulz (1991), who used random square waves to represent the concentration oscillations. Such waves were also used by Schulz *et al*. (1991) to quantify the time constant of the "intensity of segregation" (as defined by Corrsin 1957, 1964), relating it to the gas transfer across the water surface. The theme was revisited by Janzen (2006), who

compared LIF measurements with theoretical predictions, and studied the role of diffusive and turbulent transport in concentration boundary layers. Schulz and Janzen (2009) showed that the profiles of the rms concentration fluctuations and the mean concentration are related to each other, which follows from the fact that the random square wave approximation needs only a finite number of basic parameters to express the statistical variables of the turbulence transport equations. As a result, it is possible to "close" the turbulence equations, limiting their number by the number of basic parameters used. This paper presents (1) basic definitions used in the random square wave approximation, (2) the derivation of statistical variables of the mass transfer equations using the random square wave approximation and the basic parameters, and (3) an example application for the one-dimensional interfacial mass transport.

2. Turbulence transport equations and closure problem

The one-dimensional turbulent mass transfer, without sources/sinks, is usually expressed as:

$$\frac{\partial \overline{C}}{\partial t}=\frac{\partial}{\partial z}\left(D\frac{\partial \overline{C}}{\partial z}-\overline{\omega c}\right) \tag{1}$$

$\overline{C}$ and c are the mean concentration and the concentration fluctuation, respectively. ω is the vertical velocity fluctuation, t is the time, z is the vertical coordinate and D is the diffusion coefficient. Eq. (1) has two dependent variables: $\overline{C}$ (a mean profile) and $\overline{\omega c}$ (a covariance). To obtain a solution, a second equation involving the same variables is needed, but any new equation adds new unknown statistical variables, such that the obtained system is never closed (closure problem). Considering the central moments of the concentration fluctuations, $\overline{c^\theta}=\overline{[C-\overline{C}]^\theta}$, $\theta=1, 2, 3, ...$, their one-dimensional equations may be presented as:

$$\frac{1}{\theta}\frac{\partial \overline{c^\theta}}{\partial t}+\overline{c^{\theta-1}}\frac{\partial \overline{C}}{\partial t}+\overline{c^{\theta-1}\omega}\ \frac{\partial \overline{C}}{\partial z}+\frac{1}{\theta}\frac{\partial \overline{\omega c^\theta}}{\partial z}=D\left(\overline{c^{\theta-1}}\frac{\partial^2 \overline{C}}{\partial z^2}+\overline{c^{\theta-1}\frac{\partial^2 c}{\partial z^2}}\right) \tag{2}$$

$\theta=1$ reproduces Eq. (1). As can be seen, the set of Eqs. (2) involve $\overline{C}$ and $\overline{\omega c}$, but also other new unknowns. The random square waves are used here to obtain a closed set of equations.

3. Basic Definitions

Assume that the concentration $C(z, t)$ of Figure 1 oscillates between $C_p(t)$ and $C_n(t)$ in a region $z_1 < z < z_2$. Turbulence is stationary. The mean profile $\overline{C}(z, t)$

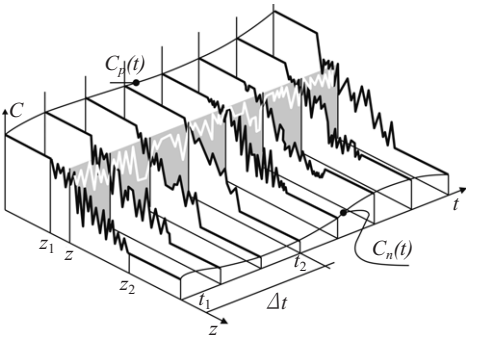

Figure 1 Sketch of a region in which C oscillates between C_p and C_n. Turbulence is stationary.

for any z in $z_1 < z < z_2$ is defined as

$$\overline{C}(z,t)=\frac{1}{\Delta t}\int_{t_1}^{t_2} C(z,t)dt \tag{3}$$

where $\Delta t=t_2, t_1$. Any statistical variables, like the central moments $\overline{c^{\theta}}=\overline{[C-\overline{C}]^{\theta}}$, are defined similarly. The same procedure is extended to the velocity field in this region. To simplify notation, both coordinates (z, t) are dropped off in the rest of the text.

3.1 Partition functions

Figure 2a is a sketch of the record of C at the position z of Figure 1. The mean value $\overline{C}(z)$ for $t_1 < t < t_2$ is also shown. The evolution of C in Figure 2a depends on turbulent transport and diffusion. Without diffusion, C would ideally alternate between C_p and C_n, as shown in Figure 2b. Diffusion transfers mass between regions with different concentrations, which, for small patches of fluid, will decrease the amplitude of the oscillations. This is shown in Figure 2c using (C_p-P) and (C_n+N), where P and N depend on z. $\overline{C}(z)$ remains unchanged.

Defining n as the fraction of the time for which the system is at the C_p-P value, we have

$$n=\frac{t\ at(C_p-P)}{\Delta t\ of\ the\ observation} \quad \text{and} \quad 1-n=\frac{t\ at(C_n+N)}{\Delta t\ of\ the\ observation} \tag{4}$$

Taking mass conservation into account leads to

$$N=\frac{Pn}{(1-n)} \tag{5}$$

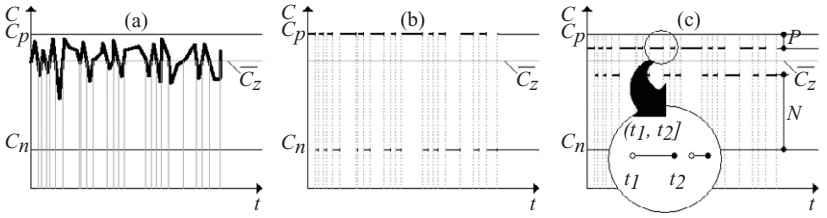

Figure 2 a) C record of figure 1 at z, b) Simplified record alternating C between C_p and C_n, c) Simplified record with amplitude damping. Upper and lower points do not superpose at the discontinuities (the C segments are open at the left and closed at the right).

n is named shortly "partition function", and is a function of the distance to the surface (z).

Eqs. (4) and (5) furnish the mean concentration profile, $\overline{C}$, as:

$$\overline{C}=nC_p+(1-n)C_n \tag{6}$$

It follows that n is given by

$$n=\frac{\overline{C}-C_n}{C_p-C_n} \tag{7}$$

Thus, the function n defined by Eq. (4) is also the normalized $\overline{C}$ profile given by Eq. (7). Following Eq. (6) for a general variable Q related to the concentration record (for example, a power of the concentration fluctuations c^{θ}), the mean value is given by

$$\overline{Q}=nQ_p+(1-n)Q_n \tag{8}$$

That is, the profile of Q is directly related to the profile n. Any new variable has its own partition function. In the present study two partition functions are used: n for the concentration (C) and m for the velocity (V).

3.2 Reduction coefficient functions

Figure 2c shows that $P < C_p - \overline{C}$. Thus, a reduction coefficient α_c is defined for the amplitude as

$$P=\alpha_c[C_p-\overline{C}] \qquad 0\leq\alpha_c\leq 1 \tag{9}$$

α_c is a function of z. Values of α_c close to 1 or 0 indicate stronger or weaker influence of diffusion, respectively. Experimental profiles of α_c were reported by Schulz and Janzen (2009) for air-water mass transfer. Using Eqs. (6), (7) and (9), N and P are expressed as:

$$\left.\begin{aligned} N&=\alpha_c\, n(C_p-C_n)\\ P&=\alpha_c\,(1-n)(C_p-C_n)\end{aligned}\right\} \qquad 0\le\alpha_c\le 1 \tag{10}$$

3.3 Superposition coefficient functions

Considering the division $C=\overline{C}+c$ and $V=\overline{V}+\omega$ (V and $\overline{V}$ are the instantaneous and mean velocities, respectively), the correlation coefficient function r for the fluctuations c and ω is given by

$$r=\frac{1}{\Delta t}\int_{t_1}^{t_2}\frac{\omega c}{\sqrt{\overline{v^2}}\sqrt{\overline{c^2}}}\,dt=\frac{\overline{\omega c}}{\sqrt{\overline{v^2}}\sqrt{\overline{c^2}}} \tag{11}$$

The records of ω and c can be at least partially superposed (concentration fluctuations are carried by velocity fluctuations). As done for C, a partition function m (depending on z) is defined for the upwards and downwards velocity fluctuations ω. A perfect superposition between c and ω implies $n=m$, though this is not usually the case. A superposition coefficient β is then defined so that $\beta=1.0$ implies $m=n$ (perfect superposition), and $\beta=0.0$ implies $m=1\text{-}n$ (inverse superposition). Thus, m can be expressed as:

$$m=1-(\beta+n-2\beta n) \tag{12}$$

where β is a function of z. Any new variable implies in new superposition functions. In the present study only one superposition coefficient function is used.

3.4 Fluctuations c

The random square waves used here generate two fluctuations around the mean value for each variable. From Eqs. (6), (9), and (10), the two concentration fluctuations are given by

$$c_1=(C_p-P-\overline{C})=(1-n)(C_p-C_n)(1-\alpha_c) \qquad \text{(positive)} \tag{13}$$

$$c_2=(C_n+N-\overline{C})=-n(C_p-C_n)(1-\alpha_c) \qquad \text{(negative)} \tag{14}$$

3.5 Fluctuations ω and velocity scale $\sqrt{\overline{\omega^2}}$

For the one-dimensional case, without mean motion, all the turbulent effects depend on the fluctuations ω. Figure 3 shows the definition of the velocity scale U by considering "downwards" (ω_d) and "upwards" (ω_u) fluctuations, which amplitudes are functions of z.

Using the partition function for the velocity, m, U is defined as the integration of the upper or the lower parts of the graph, as

$$U=\omega_d\, m \qquad \text{and} \qquad -U=-\omega_u(1-m) \tag{15}$$

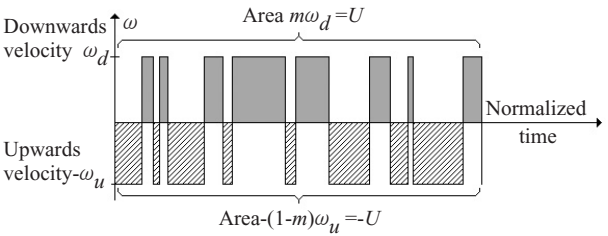

Figure 3 Upwards and downwards velocities for a fixed position z. The areas above and under the horizontal line are equal, so that the mean velocity is zero.

The mean velocity is given by $\omega_d m - \omega_u(1-m) = 0$ (or $U - U = 0$). U is a function of z ($U = 0$ at $z = 0$, where $\omega_d = \omega_u = 0$, and $U \neq 0$ for $z \to \infty$). The rms velocity $\sqrt{\overline{\omega^2}}$ is calculated as:

$$\overline{\omega^2} = m\omega_d^2 + (1-m)(-\omega_u)^2 \quad \text{and} \quad \sqrt{\overline{\omega^2}} = \sqrt{m\omega_d^2 + (1-m)(-\omega_u)^2} \tag{16}$$

From Eqs. (12), (15), and (16) it follows that

$$U = \sqrt{\overline{\omega^2}}\sqrt{[1-(\beta+n-2\beta n)](\beta+n-2\beta n)} \tag{17}$$

The velocity fluctuations are obtained from Eqs. (15) and (17):

$$\omega_d = \sqrt{\overline{\omega^2}}\sqrt{\frac{\beta+n-2\beta n}{1-(\beta+n-2\beta n)}} \quad \text{and} \quad \omega_u = -\sqrt{\overline{\omega^2}}\sqrt{\frac{1-(\beta+n-2\beta n)}{\beta+n-2\beta n}} \tag{18}$$

$\sqrt{\overline{\omega^2}}$ depends on z, being zero at the water surface and constant ($\neq 0$) in the bulk liquid. The functions n, α_c, β, and $\sqrt{\overline{\omega^2}}$ were used to obtain a closed set of equations for the one-dimensional transport.

4. Central Moments

Eq. (2) involves central moments, defined as

$$\overline{c'^{\theta}} = \overline{[C-\overline{C}]^{\theta}} \qquad \theta = 1, 2, 3, \ldots \tag{19}$$

The first order moment ($\theta = 1$) is zero. Using Eqs. (13) and (14) and the partition function n, the general central moments ($\theta = 1, 2, 3, \ldots$) are given by

$$\overline{c'^{\theta}} = c_1^{\theta} n + c_2^{\theta}(1-n) = n(1-n)[(1-n)^{\theta-1} + (-1)^{\theta}(n)^{\theta-1}](C_p - C_n)^{\theta}(1-\alpha_c)^{\theta} \tag{20}$$

or, normalizing the θ^{th} root (c'_{θ})

$$c'_{\theta}=\frac{\sqrt[\theta]{\overline{c^{\theta}}}}{(C_p-C_n)}=\sqrt[\theta]{n(1-n)[(1-n)^{\theta-1}+(-1)^{\theta}(n)^{\theta-1}]}(1-\alpha) \tag{21}$$

For $\theta=2$ we have

$$\left.\begin{aligned}&\overline{c^2}=c_1^2n+c_2^2(1-n)=n(1-n)(1-\alpha_c)^2(C_p-C_n)^2\\&c'_2=\frac{\sqrt{\overline{c^2}}}{(C_p-C_n)}=\sqrt{n(1-n)}(1-\alpha_c)\quad\text{and}\quad\alpha_c=1-\frac{\sqrt{\overline{c^2}}}{(C_p-C_n)\sqrt{n(1-n)}}\end{aligned}\right\} \tag{22}$$

Eqs. (22) were used by Schulz and Janzen (2009) to obtain α_c from experimental data. It was shown that the equation for c'_2 defines a peak amplitude lower than 0.5. Experimental data allowed to visualize how the different profiles are related, as shown by Figure 4. The gray regions represent data of Janzen (2006) on the absorption of oxygen by water, as measured in a tank with oscillating grids. c' and n are approximately linearly related for $0.4<n<1.0$.

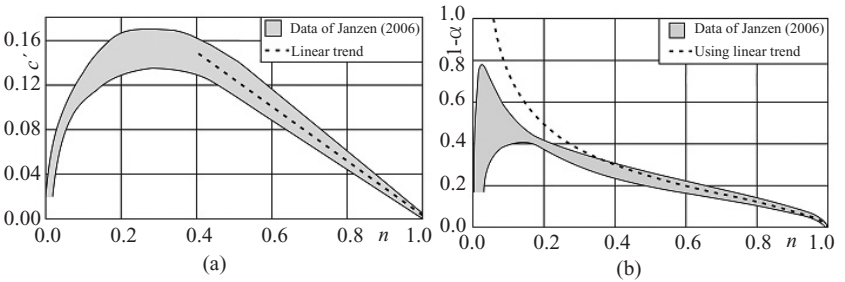

Figure 4 (a) Gray region: c' as a function of n, showing a linear dependence for $0.4<n<1.0$. (b) Gray region: 1-α_c as a function of n (- - -α_c obtained with the linear trend of figure 4a).

Eqs. (20) through (22) show that, given n and α_c, it is possible to calculate all the $\overline{c^{\theta}}$ profiles for the one dimensional transport equations.

5. Products between velocity and concentration fluctuations

5.1 Turbulent mass flux

The turbulent mass flux is defined by the mean product $\overline{\omega c}$. Thus Eq. (1) involves the turbulent mass flux along z. Janzen (2006) and Herlina and Jirka (2008) measured turbulent fluxes showing large oscillations, which points to the convenience of having $\overline{\omega c}$ expressed as function of more stable statistical profiles. Eq. (11) defines r as the correlation between ω and c, being $0<|r|<1$. But r is also the normalized mass flux, and the random square waves were used here to relate r to other statistical profiles for mass transfer.

5.2 Correlation coefficient functions

For products between powers of c and ω, the superposition coefficient β (Eq. 12) must be used to account for "imperfect" superpositions. The turbulent mass flux $\overline{\omega c}$ is given by

$$\overline{\omega c}=\omega_d[c_1 n\beta+c_2(1-n)(1-\beta)]+\omega_u[c_1 n(1-\beta)+c_2(1-n)\beta] \tag{24}$$

Eqs. (11), (13), (14), (18) and (24) lead to

$$\overline{\omega c}=\frac{n(1-n)(1-\alpha_c)\sqrt{\overline{\omega^2}}(C_p-C_n)}{\sqrt{n(1-n)+\dfrac{\beta(1-\beta)}{(2\beta-1)^2}}} \quad \text{and}$$

$$r|_{\omega,c}=\frac{\overline{\omega c}}{\sqrt{\overline{\omega^2}}\sqrt{\overline{c^2}}}=\sqrt{\frac{n(1-n)}{n(1-n)+\dfrac{\beta(1-\beta)}{(2\beta-1)^2}}} \tag{25}$$

Following the same procedure, for general θ we obtain

$$r|_{\omega,c^\theta}=\frac{\overline{\omega c^\theta}}{\sqrt{\overline{c^{2\theta}}}\sqrt{\overline{\omega^2}}}=\sqrt{\frac{n(1-n)}{n(1-n)+\dfrac{\beta(1-\beta)}{(2\beta-1)^2}}}\left\{\frac{[(1-n)^\theta-(-n)^\theta]}{\sqrt{[(1-n)^{2\theta-1}+(-1)^{2\theta}(n)^{2\theta-1}]}}\right\} \tag{26}$$

Eq. (26) shows that the normalized fluxes of c^θ depend only on n and β, while the products $\overline{\omega c^\theta}$ depend on n, β, α_c and $\sqrt{\overline{\omega^2}}$ (using Eq. 22). For $\beta = 1$ (perfect superposition), $\overline{\omega c}=\sqrt{\overline{\omega^2}}\sqrt{\overline{c^2}}$, and an "ideal" turbulent flux is obtained from the product between the rms concentration and velocity profiles. Figure 5 was obtained with data of Janzen (2006), where W is the maximum measured vertical rms velocity. The mass flux vanishes at the bottom of the tank, accumulating oxygen in the bulk liquid, so that $\overline{\omega c}$ also approaches zero in the bulk liquid.

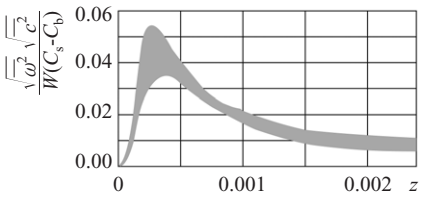

Figure 5 "Ideal" turbulent fluxes obtained from Eqs. 25 for $\beta=1$. The gray region corresponds to the envelope of the data of Janzen (2006)

6. Derivatives

Eqs. (1) and (2) also involve derivatives of mean variables. For interfacial mass transfer, C_p is the saturation concentration of the gas and C_n is the homogeneous bulk liquid gas concentration. The p^{th}-order derivative $\frac{\partial^p \overline{C}}{\partial z^p}$, is obtained from Eq. (6), as

$$\frac{\partial^p \overline{C}}{\partial z^p} = (C_p - C_n)\frac{\partial^p n}{\partial z^p} \tag{27}$$

For water bodies with the surface exposed to the atmosphere, the time evolution of the mass concentration in the bulk liquid is usually given by (see, for example, Wilhelms and Gullliver, 1991; Jähne and Monahan, 1995; Donelan *et al*. 2002)

$$\frac{dC_n}{dt} = K(C_p - C_n) \tag{28}$$

where K is the mass transfer coefficient. The dependence of K on turbulent parameters is discussed, for example, by Janzen *et al*. (2006, 2010). n depends on the agitation conditions of the liquid phase, maintained constant along the time (stationary turbulence). Thus, n does not depend on time, and the time derivative $\frac{\partial \overline{C}}{\partial t}$, obtained from Eqs. (6) and (28), is given by

$$\frac{\partial \overline{C}}{\partial t} = \frac{\partial [nC_p + (1-n)C_n]}{\partial t} \quad \text{or} \quad \frac{\partial \overline{C}}{\partial t} = K(1-n)(C_p - C_n) \tag{29}$$

Using Eq. (28), the time derivatives of the central moments $\overline{c^\theta}$ are given by:

$$\frac{\partial \overline{c^\theta}}{\partial t} = -\theta Kn(1-n)[(1-n)^{\theta-1} + (-1)^\theta (n)^{\theta-1}](C_p - C_n)^\theta (1-\alpha_c)^\theta \tag{30}$$

6.1 Products of fluctuations and derivatives

From Eqs. (13) and (14), it follows that the mean value of $\overline{c^\theta \frac{\partial^2 c}{\partial z^2}}$ is given by

$$\overline{c^\theta \frac{\partial^2 c}{\partial z^2}} = \left\{(1-n)^{\theta-1}\frac{\partial^2[(1-n)(1-\alpha_c)]}{\partial z^2} + (-n)^{\theta-1}\frac{\partial^2[-n(1-\alpha_c)]}{\partial z^2}\right\} n(1-n)(1-\alpha_c)^\theta (C_p - C_n)^{\theta+1} \tag{31}$$

As can be seen, the mean products between powers of c and its derivatives are expressed as functions of n and α_c only.

7. Applying the random square wave to mass conservation equations

All the statistical quantities existing in the one-dimensional Eqs. (1) and (2) may be expressed as dependent on the basic parameters n, β, α_c and $\sqrt{\overline{\omega^2}}$. The relationships between the statistical quantities and the basic parameters are nonlinear, so that the obtained differential equations are also nonlinear.

7.1 Equations for one-dimensional transport

Eqs. (1), (25), (27), and (29), lead to the transformed equation (substituting Eq. 1)

$$K(1-n)=D\frac{d^2n}{dz^2}-\frac{d}{dz}\left\{n(1-n)\frac{(1-\alpha_c)\sqrt{\overline{\omega^2}}}{\sqrt{n(1-n)+\dfrac{\beta(1-\beta)}{(2\beta-1)^2}}}\right\} \tag{32a}$$

The general transformed Eq. (2), using the results of the previous sections, is given by

$$\begin{aligned}
&-Kn(1-n)[(1-n)^{\theta-1}+(-1)^{\theta}(n)^{\theta-1}](1-\alpha_c)^{\theta}+\\
&+Kn(1-n)^2[(1-n)^{\theta-2}+(-1)^{\theta-1}(n)^{\theta-2}](1-\alpha_c)^{\theta-1}+\\
&+\sqrt{\frac{[n(1-n)]^{3-\theta}}{n(1-n)+\dfrac{\beta(1-\beta)}{(2\beta-1)^2}}}[(1-n)^{\theta-1}-(-n)^{\theta}][n(1-n)]^{(\theta-1)/2}\sqrt{\overline{\omega^2}}(1-\alpha_c)^{\theta-1}\frac{\partial n}{\partial z}+\\
&+\frac{1}{\theta}\frac{\partial}{\partial z}\left\{\sqrt{\frac{[n(1-n)]^{2-\theta}}{n(1-n)+\dfrac{\beta(1-\beta)}{(2\beta-1)^2}}}[(1-n)^{\theta}-(-n)^{\theta-1}][n(1-n)(1-\alpha_c)^2]^{\theta/2}\sqrt{\overline{\omega^2}}\right\}=\\
&=Dn(1-n)[(1-n)^{\theta-2}+(-1)^{\theta-1}(n)^{\theta-2}](1-\alpha_c)^{\theta-1}\frac{\partial^2 n}{\partial z^2}+\\
&+D\left\{(1-n)^{\theta-2}\frac{\partial^2[(1-n)(1-\alpha_c)]}{\partial z^2}+(-n)^{\theta-2}\frac{\partial^2[-n(1-\alpha_c)]}{\partial z^2}\right\}n(1-n)(1-\alpha_c)^{\theta-1}
\end{aligned} \tag{32b}$$

The notationt may be simplified because β and $\sqrt{\overline{\omega^2}}$ appear always together in Eqs. (32 a and b) as a combined function B

$$B=\frac{\sqrt{\overline{\omega^2}}}{\sqrt{n(1-n)+\dfrac{\beta(1-\beta)}{(2\beta-1)^2}}} \tag{33}$$

As a consequence, only three functions remain as unknown: n, B, and α_c. To obtain a solution, a closed set of three equations is needed, given by 1) Eq. (32a), 2) Eq. (32b) for $\theta=2$, and 3) Eq. (32b) for $\theta=3$.

7.2 Example using constant $\overline{\alpha_c}$

The three coupled nonlinear equations may have no simple solution. Although the objective of this study was to *obtain* the equations, an example was also solved, in which a constant $\alpha_c=\overline{\alpha_c}$ was used. In this case, the set of Eqs. (32a) and (32b) for $\theta=2$ was used, which was reduced, through simple substitution, to the single equation for n

$$(1-A)\left(\frac{dn}{dy}\right)^2\left[\frac{d^2n}{dy^2}-\kappa(1-n)\right]=A\left\{\frac{d^3n}{dy^3}\left[-2An(1-n)-\frac{(1-2n)}{2}\right]\frac{dn}{dy}+\right.$$
$$+\frac{d^2n}{dy^2}\left\{[-2A(1-2n)+1]\left(\frac{dn}{dy}\right)^2+\left(2An(1-n)+\frac{(1-2n)}{2}\right)\frac{d^2n}{dy^2}-\right.$$
$$\left.\left.-\frac{(1-2n)}{2}(1-n)\kappa-\kappa nA(1-n)\right\}+\kappa A(1-2n)\left(\frac{dn}{dy}\right)^2-\kappa(1-n)\left(\frac{dn}{dy}\right)^2\right\} \qquad (34)$$

In this equation $\kappa=KE^2/D$, $A=1-\overline{\alpha_c}$ and $y=z/E$ are nondimensional parameters, with E being the distance $E=z_2-z_1$ of Figure 1. Eq. (34) admits analytical solutions for the extreme case A $\rightarrow$ 0 (or $\overline{\alpha_c}\rightarrow 1$), for which it reduces to $\frac{d^2n}{dy^2}=\kappa(1-n)$. But this effect of diffusion for all $0<y<1$ is considered overestimated. So, Eq. (34) was solved using the fourth order Runge-Kutta method, imposing convenient values to κ. Because it is a third order differential equation, the following system of three first order equations was generated:

$$\begin{cases}\dfrac{dn}{dy}=j,\ \dfrac{dj}{dy}=w,\ \dfrac{dw}{dy}=\dfrac{(1-A)j^2[w-K(1-n)]-Awf_1+f_2}{j\left[-2An(1-n)-\dfrac{(1-2n)}{2}\right]A} & \textit{where}\\ f_1=\left[(-2A(1-2n)+1)j^2+A\left(2An(1-n)+\dfrac{(1-2n)}{2}\right)w-\right.\\ \left.-A\dfrac{(1-2n)}{2}(1-n)K-KnA^2(1-n)\right]\\ \textit{and}\qquad f_2=j^2KA[(1-n)-A(1-2n)]\end{cases} \qquad (35)$$

Two boundary conditions were set as $n(0)=1$ and $n(1)=0$ (adequate for interfacial mass transfer). But as three boundary conditions are needed to solve the system of Eq. (35), a value for the second derivative of n at the surface, n"(0), was adjusted, allowing us to calculate $j(0)$ and $w(0)$. The Runge-Kutta method is explicit, but iterative procedures were needed to evaluate the mentioned functions

at $y=0$. The quasi-Newton method was applied using the solver tool of the Excel® table. The curve of Figure 6 was obtained for $0.001 \leq \kappa \leq 0.005$. This range was based on the k values calculated from experimental data on oxygen absorption by water obtained by Janzen (2006), which furnished ~$0.003 < \kappa <$ ~0.004. Measured boundary layer thicknesses were used for E. For the second derivative, the best value oscillated around n"$(0)=1.0$, so that this value was used (which coincides with the second derivative of $n=\exp(-y)$, a profile used for example by Herlina and Jirka, 2008). As inferred from Figure 4b, A varies in the range $0 \leq A \leq 1$. The mean value $A=0.5$ was then adopted. Even using this strong simplification (constant A), Figure 6 shows a predicted n-profile that follows the general form of the measured data. More accurate predictions must evidently consider the dependence of α_c on z, and the solution of the three coupled equations.

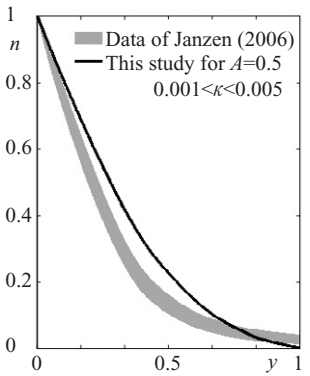

Figure 6 n for interfacial mass transfer using constant A. A single curve was calculated for $0.001 \leq \kappa \leq 0.005$. The gray region is the envelope of the data measured by Janzen (2006).

8. Conclusions

It was shown that the equations for one-dimensional mass transfer in turbulent flows may be reduced to a set of three equations involving three unknown functions, that is, a set of closed equations. The methodology followed to derive these equations used random square waves to represent the turbulent records of velocity and mass concentration. Basic definitions were introduced: the partition functions, the reduction coefficients and the superposition coefficients. The obtained transformed equations for one-dimensional mass transfer are nonlinear. To illustrate the use of the transformed equations, a solution for the partition function n was presented for interfacial mass-transfer using a mean $\alpha_c=\overline{\alpha_c}$. In this

case, the system of equations reduces to only two coupled equations, generating a single third order differential equation for n. Although this is a simplification (constant $\overline{\alpha_c}$), the predicted n profile followed the general form of measured data, pointing to the convenience of this methodology. It was also shown that for more accurate predictions, the dependence of α_c with z must be considered in the set of three equations.

Acknowledgements

The authors thanks: 1) Profs. Rivadavia Wollstein and Beate Frank (Universidade Regional de Blumenau), and Prof. Nicanor Poffo, (Conjunto Educacional Pedro II, Blumenau), for relevant advises and 2) "Associação dos Amigos da FURB", for financial support.

References

Corrsin, S. (1957), Simple theory of an idealized turbulent mixer, *AIChEJ., 3*(3), 329-330.

Corrsin, S. (1964) The isotropic turbulent mixer:part II-arbitrary Schmidt number, *AIChE J, 10*(6), 870-877.

Donelan, M.A., Drennan, W.M., Saltzman, E.S. and Wanninkhof, R. (Eds.)(2002), *Gas Transfer at Water Surfaces*, Geophysical Monograph Series, American Geophysical Union, Washington, U.S.A., 383 pp.

Herlina, H. and Jirka, G.H. (2008), Experiments on gas transfer at the air-water interface induced by oscillating grid turbulence, *J. Fluid Mech. ,594*, 183-208.

Hinze, J.O. (1959), *Turbulence*, Mc. Graw-Hill Book Company, USA, 586 pp.

Jähne, B. and Monahan, E.C. (Eds.)(1995), *Air-Water Gas Transfer*, Selected papers from the Third International Symposium on Air-Water Gas Transfer, Heidelberg, Germany, AEON Verlag & Studio, 918 pp.

Janzen, J.G. (2006), Gas transfer near the air-water interface in an oscillating-grid tanks and properties of isotropic turbulent flows (Portuguese: Fluxo de massa na interface ar-água em tanques de grades oscilantes e detalhes de escoamentos turbulentos isotrópicos oscilantes). Doctoral thesis, 170 pp., University of Sao Paulo, Brazil.

Janzen J.G, Schulz H.E., Jirka GH. (2006) Air-water gas transfer details (Portuguese: Detalhes da transferência de gases na interface ar-água). *Revista Brasileira de Recursos Hídricos*, *11*, 153-161.

Janzen, J.G., Herlina, H., Jirka, G.H., Schulz, H.E. and Gulliver, J.S. (2010) Estimation of mass transfer velocity based on measured turbulence parameters, *AIChEJ, 56*(8), 2005-2017.

Monin, A. S. and Yaglom, A. M. (1979), *Statistical Fluid Mechanics: Mechanics of Turbulence*, Vol.1, the MIT Press, 4th ed., 769pp.

Monin, A. S. and Yaglom, A. M. (1981), *Statistical Fluid Mechanics: Mechanics of Turbulence*, Vol.2, the MIT Press, 2th ed., 873pp.

Pope, S.B. (2000), *Turbulent Flows*, Cambridge University Press, 1st ed., UK, 771pp.

Schulz, H.E.; Bicudo, J.R., Barbosa, A.R. and Giorgetti, M.F. (1991), Turbulent Water Aeration: Analytical Approach and Experimental Data, *Air Water Mass Transfer* (Eds. Wilhelms, S.C. and Gulliver, J.S.), ASCE, New York, 142-155.

Schulz H. E., Schulz S. A. G. (1991) Modelling below-surface characteristics in water reaeration. *Water pollution, modelling, measuring and prediction* (Eds. Wrobel, L.C. and Brebbia, C.A.), Computational Mechanics Publications and Elsevier Applied Science, 441–454.

Schulz, H.E. and Janzen, J.G. (2009) Concentration fields near air-water interfaces during interfacial mass transport: oxygen transport and random square wave analysis. *Braz. J. Chem. Eng., 26*(3), 527-536.

Wilhelms, S.C. and Gulliver, J.S. (Eds.)(1991) *Air-Water Mass Transfer*, Selected Papers from the Second International Symposium on Gas Transfer at Water Surfaces, Minneapolis, U.S.A., ASCE, 802 pp.