Concentration Fluctuations Close to a Gas-Liquid Interface

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Sirkar and Hanratty (1970) and Shaw and Hanratty (1977) have used electrochemical techniques to obtain extensive results on mass transfer between a turbulently flowing fluid and a solid boundary for large Schmidt numbers. The most striking finding of these studies is that the characteristic frequency of the mass transfer fluctuations decreases with increasing Schmidt number and is much smaller than the frequency of the most energetic velocity fluctuations.

Campbell (1982) has recently shown that an understanding of these low frequency fluctuations is significant in defining the mechanism of mass transfer to a wall. Through numerical solutions of the unaveraged mass balance equation, he found that Reynolds transport is controlled by low frequency velocity fluctuations and that decreasing fractions of the energy of the velocity fluctuations are effective in transporting mass as the Schmidt number increases. These results present a physical picture of mass transfer at a solid boundary which is quite different from classical approaches such as the mass-momentum analogy, the Nernst diffusion layer concept, or surface renewal theory.

Therefore, it is of interest to know whether these same concepts are applicable to sheared, clean gas-liquid interfaces (Davis, 1972), which, because of their mobility, are less restrictive on the flow. It is our purpose to address this question.

The specific problem considered can arise for annular or stratified gas-liquid flows when a component from a flowing gas stream is absorbed by a concurrently flowing turbulent liquid layer whose interface does not contain an absorbed surface-active film. The primary resistance to mass transfer is in the liquid phase. Under these circumstances, the Schmidt number is large and the concentration boundary-layer in the liquid is thin. Mass transfer is controlled by properties of the fluctuating velocity field in the liquid in the immediate vicinity of the interface. A principal difference from the case of a solid boundary or of a contaminated interface is that velocity fluctuations normal to the interface vary linearly rather than quadratically with distance from the interface. We explore the consequences of this difference in the spatial variation of normal velocity fluctuations on the sensitivity of the concentration boundary-layer to high frequency velocity fluctuations.

FORMULATION AND SOLUTION

More specifically we want to calculate how changes in the Schmidt number, S, affect the frequency of the concentration fluctuations close to a boundary at which mass transfer is occurring. Sirkar and Hanratty (1970) have shown that for the case in which velocity fluctuations normal to the surface, v, are varying quadratically with distance from the surface, y, the concentration boundary-layer acts as a low pass filter in that only low frequency fluctuations in v are effective in causing concentration fluctuations. The question we want to explore is whether this also occurs when v is varying linearly with y.

To find an answer we need only consider the high frequency fluctuations, Sirkar and Hanratty (1970) have shown that these can be related to the normal velocity fluctuations by solving the linear mass balance equation,

$$\frac{\partial c}{\partial t} + v\frac{d\overline{C}}{dy} + u\frac{d\overline{C}}{dx} = \frac{1}{S}\left(\frac{\partial^2 c}{\partial x^2} + \frac{\partial^2 c}{\partial y^2} + \frac{\partial^2 c}{\partial z^2}\right) \tag{1}$$

For the specific situation being considered, the mass transfer is controlled by the shear stress at the interface, $\overline{\tau}_s$ (Aisa et al., 1981). Therefore we have made the variables in Eq. 1 dimensionless using $v^* = (\overline{\tau}_s/\rho)^{1/2}$ as a characteristic velocity, ν/v^* as a characteristic length and the concentration at the interface, $\overline{C}_s$, as a characteristic concentration. For a fully developed flow $d\overline{C}/dx \approx 0$. Since the concentration boundary-layer is very thin, $\partial^2 c/\partial y^2$ is much larger than $\partial^2 c/\partial x^2$ or $\partial^2 c/\partial z^2$. Therefore Eq. 1 can be simplified to

$$\frac{\partial c}{\partial t} + v\frac{d\overline{C}}{dy} = \frac{1}{S}\frac{\partial^2 c}{\partial y^2}\,. \tag{2}$$

A solution of Eq. 2 is to be determined for a periodically varying velocity field,

$$v = \hat{v}y\exp(i\omega t). \tag{3}$$

Because the equation is linear, the solution can be expressed in the form

$$c = \hat{c}\exp(i\omega t). \tag{4}$$

If Eqs. 3 and 4 are substituted into Eq. 2 the following equation for $\hat{c}$ is obtained:

$$\frac{d^2\hat{c}}{dy^2} - n^2\hat{c} = \hat{v}Sy\frac{d\overline{C}}{dy}\,, \tag{5}$$

where $n^2 = i\omega S$. The solution to Eq. 5 satisfying the boundary conditions

$$\begin{aligned} &\hat{c} = 0, \quad \overline{C} = 1 \quad && \text{at } y = 0 \\ &\hat{c} = 0, \quad \overline{C} = 0 \quad && \text{at } y = \infty, \end{aligned} \tag{6}$$

is obtained using a variation of parameters technique.

$$\begin{aligned} \frac{\hat{c}}{S\hat{v}} = &-\frac{1}{2n}e^{-ny}\left[\int_0^y e^{nyy}\frac{d\overline{C}}{dy}dy\right] \\ &+\frac{1}{2n}e^{-ny}\left[\int_0^\infty e^{-nyy}\frac{d\overline{C}}{dy}dy\right] \\ &-\frac{1}{2n}e^{ny}\left[\int_y^\infty e^{-nyy}\frac{d\overline{C}}{dy}dy\right]\,. \end{aligned} \tag{7}$$

The amplitude of the dimensionless fluctuating mass transfer coefficient is defined as

$$\hat{k} = -\frac{1}{S}\frac{d\hat{c}}{dy}\bigg|_{y=0}. \tag{8}$$

From Eqs. 7 and 8 we obtain

$$\hat{k} = -\hat{v}\int_0^\infty e^{-ny}\left(y\frac{d\overline{C}}{dy}\right)dy \tag{9}$$

In order to evaluate Eq. 9 it is necessary to specify $d\overline{C}/dy$. We assume the eddy diffusivity varies as y^2 near a mobile interface and this leads to

$$\frac{d\overline{C}}{dy} = \frac{\overline{K}}{\frac{1}{S} + ay^2}\,, \tag{10}$$

where

$$\overline{K} = -\frac{1}{S}\frac{d\overline{C}}{dy}\bigg|_{y=0}. \tag{11}$$

Using these two equations the integral (Eq. 9) becomes

$$\hat{k} = -\hat{v}\int_0^{\infty} e^{-ny}y \frac{\overline{K}}{\left(\frac{1}{S} + ay^2\right)} dy. \tag{12}$$

Integration by parts yields a power series in $1/n^2$. The first term, which will dominate if $\omega > 0.01$ for $S \approx 500$, is

$$\frac{\hat{k}}{\overline{K}} = \frac{\hat{v}S}{n^2}. \tag{13}$$

Since

$$\frac{\hat{k}\hat{k}^{\ddagger}}{\overline{K}^2} = \frac{\hat{v}\hat{v}^{\dagger}S^2}{n^2 n^{\dagger 2}}, \tag{14}$$

where the dagger denotes the complex conjugate, the following relation between the frequency spectra for the mass transfer fluctuations and the normal velocity fluctuations is obtained:

$$\frac{W_k(\omega)}{\overline{K}^2} = \frac{W_v(\omega)}{\omega^2}. \tag{15}$$

The above result is insensitive to the choice of $d\overline{C}/dy$. For example, if we take

$$\overline{C} = \exp(-\overline{K}Sy), \tag{16}$$

then Eq. 12 yields

$$\frac{W_k(\omega)}{\overline{K}^2} = \frac{W_v(\omega)S^2}{(S\overline{K} + n)^2(S\overline{K} + n^{\dagger})^2}. \tag{17}$$

For large n this is identical to Eq. 15.

A similar analysis can be performed for a fluid-solid boundary. In this case we take

$$v = \hat{v}y^2 \exp(i\omega t). \tag{18}$$

The solution this time is a series in $1/n^3$ and the first term, which again will dominate is

$$\frac{\hat{k}}{\overline{K}} = \frac{2\hat{v}S}{n^3}. \tag{19}$$

The relation between the two spectra is

$$\frac{W_k(\omega)}{\overline{K}^2} = \frac{4W_v(\omega)}{\omega^3 S}, \tag{20}$$

which is the result previously obtained by Sirkar and Hanratty (1970).

DISCUSSION

The appearance of the Schmidt number in the denominator of Eq. 20 decreases the effectiveness of the turbulence in causing mass transfer fluctuations. Thus the frequency required to obtain some fixed value of $W_k(\omega)/\overline{K}^2$ decreases with increasing S.

As can be seen from Eq. 15, this damping effect is not present for the case of a mobile interface. We therefore conclude that at large Schmidt numbers high frequency velocity fluctuations are playing a more important role in transporting mass at a clean gas-liquid interface than at a solid-liquid interface.

This calculated strong influence of the spatial variation of the normal velocity fluctuations provides a physical interpretation of the filtering effect of the concentration boundary-layer close to a solid surface. From Eq. 2, it is seen that concentration fluctuations close to a solid boundary are caused by the term $v d\overline{C}/dy$. As the Schmidt number increases, the concentration boundary layer becomes thinner and the derivative $d\overline{C}/dy$ increases. However, if $v \sim y^2$, the amplitude of the velocity fluctuations in the concentration boundary-layer decreases much more rapidly than $d\overline{C}/dy$ increases with increasing Schmidt number. In order for a fluctuation in $v d\overline{C}/dy$ to cause an appreciable fluctuation in the concentration its duration must increase if the Schmidt number increases. Consequently, as the Schmidt number increases, the effective velocity fluctuations are of lower frequency; i.e., the high frequencies are filtered.

CONCLUSIONS

The analysis presented above provides a physical interpretation of how the concentration boundary-layer can act as a low pass filter at high Schmidt numbers. It shows that, if the velocity fluctuations normal to the surface increase more rapidly with distance from the surface than linearly, concentration fluctuations are caused by low frequency velocity fluctuations.

This result indicates a fundamental difference between the concentration field close to a clean sheared interface and the concentration field close to a solid boundary or to a sheared interface with a surface film, which had not been previously observed. The filtering action of the concentration boundary-layer is much less effective for a clean gas-liquid interface and consequently high frequency fluctuations can have an important influence on mass transfer. As indicated from calculations presented by Campbell (1982), a physical understanding of the difference in mass transfer results for clean gas-liquid interfaces from those for interfaces with surface films cannot be obtained without taking this filtering into account.

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NOTATION

a	= coefficient for the eddy diffusivity relation
$\overline{C}$	= time averaged dimensionless concentration
$\overline{C}_S$	= time averaged interfacial concentration
c	= fluctuating, dimensionless concentration
$\overline{K}$	= time averaged mass transfer coefficient
k	= fluctuating mass transfer coefficient
n	= $\sqrt{i\omega S}$
S	= Schmidt number
t	= dimensionless time
v	= fluctuating velocity normal to interface
v^*	= friction velocity = $(\overline{\tau}_s/\rho)^{1/2}$
W_k	= $\hat{k}\hat{k}^{\dagger}$
W_v	= $\hat{v}\hat{v}^{\dagger}$
y	= distance normal to interface

Greek Letters

ρ	= liquid density
ω	= dimensionless frequency
ν	= kinematic viscosity
$\overline{\tau}_s$	= time averaged shear stress at the interface

Other Symbols

i	= $\sqrt{-1}$
$\hat{}$	= amplitude of
$\dagger$	= complex conjugate of

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