A modification of the film model

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ABSTRACT:

We consider a composite film/penetration model; for simplicity of exposition we describe this only for the single component (scalar) case. Thus, we have a 'film' of fluid (adjacent to an interface — say, the gas/fluid interface of a bubble) whose thickness has been normalized to 1 so we take the variable

$x \in [0,1]$ with $x = 0+$ representing this interface. To the other side of $x = 1$ is 'bulk fluid' and our assumption is that this bulk fluid is well-mixed while the primary transport within the film is by diffusion. Our principal concern here is with modeling of the interaction between the film and the bulk. We consider, respectively, the concentration profile $u = u(x)$ within the film and the concentration U in the bulk fluid for some (single) solute of interest.

For the standard film model (Nernst transport theory, see, e.g., [1]), one has a diffusive flux in the film (Du_x by Fick's Law) and a sharp film boundary at which concentrations match $[u\big|_{x=1} = U]$ with the flux out of the film at $x = 1$ providing a source term $\sigma\left[-Du_x\big|_{x=1}\right]$ for the evolution of U (where σ is a geometric normalization constant). The evolution equations are then

$$
\begin{array}{rcl}
\dot{u} & = & [Du_x]_x + f(u) \\
\dot{U} & = & \sigma\left[-Du_x\big|_{x=1}\right] + F(U) \\
u\big|_{x=1} & = & U
\end{array}
\tag{1}
$$

with, of course, initial conditions for u, U and a boundary condition for u at $x = 0$; here, f, F are suitable reaction (source) terms. Note that this involves no interaction at all between the film concentration and the bulk except for the matching condition at $x = 1$.

Physically, it is reasonable for a well-stirred liquid to have an effectively stationary boundary layer adjacent to an interface. However, a notion like 'well-stirred' suggests a turbulent flow pattern for which a sharp film boundary, as above, is somewhat unreasonable. On a stochastic basis, one would expect random interaction (material exchange) between the fluid of the film and penetrating eddies of bulk fluid. It is this which we attempt to model here, assuming the random fluctuations are on a rapid enough time-scale that we may average them out for a deterministic theory.

Ideas of the same kind have been discussed previously in the literature, for instance in the surface renewal theory [4]. Similar explanations have also been presented for the enhancement of the gas–absorption rate due to solid particles; see [5] for a recent reference. Instead of using the residence time or residence time distributions of the interface volume elements, we derive the additional transport term from a probabilistic point of view. Here, we only give a formal presentation with a synthetic numerical example, and do not attempt to correlate the model with real physical properties of the gas/liquid system.

Proceeding along the lines above, we assume that one has, effectively, a Poisson distribution of 'interaction events' — that is, for some $\gamma = \gamma(x) \geq 0$ one has[1]

$$\textbf{Prob}\,\{\,\text{'material exchange' in } dx \text{ during } dt\,\} = \gamma dx dt \tag{2}$$

where we assume independence between non-overlapping dt. Neglecting here any consideration of the diffusion or reaction, the expected value of $u(t+dt)$ (within $[x, x+dx]$) is then given by

$$\begin{aligned}
\textbf{Prob}\,\{\,\text{no exchange}\,\} \cdot u(t,x) + \textbf{Prob}\,\{\,\text{exchange}\,\} \cdot U(t)& \\
= \quad & [1-\gamma dt]u(t,x) + [\gamma dt]U(t) \\
= \quad & u(t,x) - \gamma[u-U]dt
\end{aligned}$$

whence

$$\textbf{Expectation}\left[\frac{u(t+dt)-u(t)}{dt}\right] = -\gamma[u-U].$$

Thus, this just adds a term $-\gamma[u-U]$ in $\dot{u}$ to the earlier consideration of reaction and diffusion in (1) so including this form of material transport gives us the new evolution system:

$$\begin{aligned}
\dot{u} &= [Du_x]_x + f(u) - \gamma[u-U] \\
\dot{U} &= \sigma\left[-Du_x\Big|_{x=1} + \textstyle\int_0^1 \gamma[u-U]\,dx\right] + F(U) \\
u\Big|_{x=1} &= U.
\end{aligned} \tag{3}$$

From our discussion of the model, it is clear that we should expect $\gamma(\cdot)$ to be an increasing function of x since penetration occurs 'from the right'. [This, of course, also means that it would be unreasonable to have assumed independence of the events for nonoverlapping dx; fortunately that was not used in the probabilistic analysis above, leading to (3).]

The well–posedness of the model has been established in [2]. We note here that the additional interaction term does not change the essential behavior of the system (such as the long time behavior, etc.) with reasonable reaction terms f, F.

[1] It is also worth noting another interpretation of the parameter γ: it is a well-known fact of the theory of Poisson processes that the expected time between these interaction events within dx is just $1/[\gamma dx]$.

At this point we note that u will be a smooth function of x on the interval $(0, 1)$ so the condition that $\gamma(u-U)$ be integrable automatically means that:

$$
\begin{array}{rcl}
\gamma \text{ not integrable at } 1- & \Rightarrow & u\Big|_{x\to 1} = U, \\
(1-x)\gamma \text{ not integrable at } 1- & \Rightarrow & u_x\Big|_{x\to 1} = 0.
\end{array}
\tag{4}
$$

We suppose that $\gamma(\cdot)$ is increasing and otherwise 'nice' on $[0, 1)$. If we recall the interpretation of $1/\gamma$ above, we realize that the perfect mixing in the bulk fluid might be interpreted as having $1/\gamma \equiv 0$ for $x > 1$. Our current viewpoint of a 'fuzzy' boundary 'near' $x = 1$ certainly suggests that $\gamma \to \infty$ as $x \to 1$ and it is entirely reasonable to ask also that $(1-x)\gamma$ not be integrable. From (4), this would mean that the boundary condition $u = U$ at $x = 1$ can be omitted and that the boundary flux term $-\sigma D u_x$ in the equation for U can also be omitted. A plausible specific choice for γ would be

$$
\gamma(x) = C \tan^2\left(\frac{\pi x}{2}\right)
\tag{5}
$$

which behaves appropriately both near $x = 1-$ and near $x = 0+$.

We present a simple nondimensional numerical example. Consider a single gas component u diffusing into the liquid. The surface concentration of u as well as the volume of the liquid are taken normalized to the value one. With the (rather arbitrary) values $D = 0.5$, $\sigma = 0.2$ and the film thickness assuming the value 0.25, we integrate the system 3 to the steady state $u = U = 1$. In order to see the effect of the γ term, we perform the calculation with the two choices

$$
\begin{array}{rcl}
\gamma(x) & \equiv & 0 \quad \text{[This is just the original film model.]} \\
\gamma(x) & = & 100 \tan^2\left(\frac{\pi x}{2}\right)
\end{array}
\tag{6}
$$

For simplicity, we consider pure mass transport, with $f = F = 0$.

The figures below show the results. Figure 1 exhibits the film profiles for the two cases [film model $\leftrightarrow$ solid line; new model (i.e., (5) with $C = 100$) $\leftrightarrow$ dashed line]. These are shown for the time points $t = 0.53, 1.05, 1.58, 2.10, 2.63$, observing that the concentrations $u(\cdot)$ are increasing in t. We note that the present model involving γ annihilates the artificial sharp boundary at $x = 1$, present in the standard film model — noting that the 'actual' profile is given by extending the graph to the right as a constant ($= U$). With the value

$C = 100$ used here, one observes an enhanced mass transfer (i.e., higher values of U) in the comparison but this is not an intrinsic feature of the model and the choice of the parameter C obviously should require a fit to data. Figure 2 gives the solutions for the bulk concentration U for $0 < t < 10$, approaching the equilibrium value of 1; cf., [2].

These solutions were computed using the numerical 'method of lines', as presented, e.g., in [3]. The addition of the γ term does not significantly increase the computation times.

References

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