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TECHNICAL NOTES

The effect of diffusivities ratio on conjugate mass transfer from a droplet

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INTRODUCTION

SO FAR theoretical studies concerning the unsteady mass transfer from a fluid particle moving in another fluid dealt only with two limiting cases, for which the rate of mass transfer is controlled by the resistance either of the dispersed phase (the internal problem) or of the continuous phase (the external problem). But in many cases, especially in liquid–liquid systems, the transfer resistance of both phases are comparable (the conjugate problem). Illuminate discussion concerning these problems can be found in refs. [1, 2].

Except for the $Pe = 0$ (stagnant phases) situation, solved numerically by Plöcher and Schmidt-Traub [3] and analytically by Cooper [4], "there are no general solutions for the case where the transient resistances in both phases are significant" [2].

The most simple and direct way to treat the $Pe \neq 0$ situation is the well-known principle of resistance additivity. Experiments in this sense, together with confrontations with experimental data can be viewed in refs. [5–7]. Otherwise, two types of approximate solutions have been given for the $Pe \neq 0$ case:

(1) The first, due to Ruckenstein [8] and Chao [9], assumes thin concentration boundary layers on both sides of the interface, and we shall call it 'the boundary layer approximation' (BLA).

(2) In the second, presented by Brounshtein *et al.* [10] and Clift *et al.* [2], internal mass transfer is described by the same partial differential equation of Kronig and Brink for the circulating droplet, but the boundary condition at the interface takes into consideration the resistance of the continuous phase; the external Sherwood number is assumed to be known and equal to its steady value; we shall call this solution 'the quasi-internal approximation' (QIA).

Recently, Abramzon and Borde [1] gave a numerical solution to the conjugate problem for $Pe \neq 0$, but they used the assumption of equal diffusivities in both phases. Iyengar [11], using the von Neumann method proves that their numerical method can be locally unstable, but it does not find a real mesh point where the product $F_1 \cdot F_2 > 1$ (for F_1 and F_2 see the notation used in ref. [11]). Note that on the frontier domain, the Iyengar analysis is not valid due to the treatment of the boundary conditions followed by Abramzon and Borde [1]. Our aim is to extend the analysis presented in ref. [1] by taking into consideration the effect of diffusivities ratio on mass transfer.

MATHEMATICAL MODEL

Consider a spherical droplet of radius a, moving slowly, $Re < 1$, into an unbound volume of another liquid. Common assumptions are:

(a) the flow fields inside and outside of the droplet are steady and axisymmetric;

(b) during mass transfer the physical properties of the fluid within the particle and in the surrounding medium and the droplet shape and volume remain constant.

With these assumptions the unsteady conjugate mass transfer equation in dimensionless form with proper initial and boundary conditions reads as follows:

$$\frac{\partial Z_i}{\partial \tau_i} + \frac{Pe_i}{2}\left(V_{R,i}\frac{\partial Z_i}{\partial r} + \frac{V_{\theta,i}}{r}\frac{\partial Z_i}{\partial \theta}\right) = \frac{1}{r^2}\frac{\partial}{\partial r}\left(r^2\frac{\partial Z_i}{\partial r}\right) + \frac{1}{r^2 \sin\theta}\frac{\partial}{\partial \theta}\left(\sin\theta\frac{\partial Z_i}{\partial \theta}\right) \quad (1)$$

$$Z_1(r,\theta,0) = 1.0, \quad Z_2(r,\theta,0) = 0 \quad (2)$$

$$Z_1(0,\theta,\tau_1) < \infty \quad (3)$$

$$D_1\left.\frac{\partial Z_1}{\partial r}\right|_{r=1} = D_2\left.\frac{\partial Z_2}{\partial r}\right|_{r=1} \quad (4)$$

$$Z_1(1,\theta,\tau_1) = H \cdot Z_2(1,\theta,\tau_2) \quad (5)$$

$$\frac{\partial Z_i}{\partial \theta}(r,0,\tau_i) = \frac{\partial Z_i}{\partial \theta}(r,\pi,\tau_i) = 0. \quad (6)$$

Here subscript i is equal to 1 for the dispersed phase and 2 for the continuous phase. The velocity components are those derived by Hadamard and Rybczynski and presented in ref. [8].

METHOD OF SOLUTION

We solved this problem numerically by an implicit finite difference technique. The radial coordinate r for the outer region was replaced by x using the transformation $r = \exp x$.

For sufficiently large Pe numbers we are in the situation when convection dominates diffusion, or more generally speaking we have a singular perturbation problem. In this case the discretization of first-order terms by a centred difference scheme of second-order accuracy has an intrinsically unstable character which exhibits oscillations, negative concentrations, overshooting, etc. [12].

The remedy, which is not always valid, is the reduction of time and/or space stepsize, but this leads to an uneconomical solver. To overcome all these difficulties, special discretization schemes have been proposed [13, 14] (and references quoted therein). From all these we select the exponentially fitted scheme [14].

A decomposition procedure of ADI type [15], which necessitates at every time step the solution of a tridiagonal system is used. If we split the spatial operator of equation (1), L, into an r component and a θ component, L_r and L_θ, using the exponentially fitted scheme both the discrete projections of L_r and L_θ are of positive type (for L, L_r and L_θ see nomenclature). Thus from ref. [15] results that our numerical scheme is stable for any value of the time step $\Delta\tau > 0$.

NOMENCLATURE

a	sphere radius
C	concentration of transferring component
D	diffusivity
H	equilibrium constant
k	viscosities ratio, μ_1/μ_2
L	differential operator, $1/r^2\, \partial/\partial r(r^2 \partial/\partial r) + 1/r^2 \sin\theta\, \partial/\partial\theta\, (\sin\theta\, \partial/\partial\theta) - Pe/2\, (V_R\, \partial/\partial r + V_\theta/r\, \partial/\partial\theta)$
L_r	differential operator, $1/r^2\, \partial/\partial r\, (r^2 \partial/\partial r) - Pe/2\, (V_R\, \partial/\partial r)$
L_θ	differential operator, $1/r^2 \sin\theta\, \partial/\partial\theta\, (\sin\theta\, \partial/\partial\theta) - Pe/2\, (V_\theta/r\, \partial/\partial\theta)$
Pe	Peclet number, $2aU/D$
R	distance from the centre of the sphere
r	dimensionless radial coordinate, R/a
Re	Reynolds number, $2aU\rho/\mu$
Sh	over Sherwood number defined by equation (8) or equation (9)
t	time
U	free-stream fluid velocity
V_R	radial velocity component
V_θ	tangential velocity component
Z	dimensionless concentration, $(C-C_\infty)/(C_0-C_\infty)$.

Greek symbols

θ	polar angle, spherical coordinate system
μ	dynamic viscosity
ρ	density
τ	dimensionless time, tD/a^2.

Subscripts

ex	external problem
i	1 refers to dispersed phase, 2 refers to continuous phase
in	internal problem
s	droplet surface
0	initial condition
∞	large distance from the spherical particle.

The solution of both internal and external problems are needed in our paper. The same method was used. The asymptotic Sherwood number was computed by integration on long times. Otherwise, the asymptotic external Sherwood number can be computed by solving the pure elliptic problem derived from equation (1). The discretization procedure was the same. The resultant linear algebraic system was solved by a full-fas multigrid algorithm [16]. As recommended by Hackbusch [17], an incomplete lower–upper decomposition method [18] (the *EQ* variant) was used like a smoothing step. The nine point prolongation and restriction operators were used for the transfer of residuals [17]. The iteration cycle was stopped when dynamical residuals dropped the truncation error [19]. The multigrid worked very well even at greater *Pe* numbers than those used in the present study.

As usual the results are summarized in terms of:

(a) average particle concentration

$$\bar{Z}_1 = \frac{3}{2}\int_0^1 r^2\left(\int_0^\pi Z_1 \sin\theta\, d\theta\right) dr; \tag{7}$$

(b) overall instantaneous Sherwood number

$$Sh_i = \frac{\dfrac{D_i}{D_2}\displaystyle\int_0^\pi \left.\frac{\partial Z_2}{\partial r}\right|_{r=1} \sin\theta\, d\theta}{\bar{Z}_1}. \tag{8}$$

By taking the difference between the mixed mean particle concentration and the concentration of the surrounding medium far from the droplet as a driving force, the Sherwood number may be calculated from the mass balance equation for the droplet by

$$Sh_i = -\frac{2}{3}\frac{D_i}{D_1}\frac{d\ln\bar{Z}_1}{d\tau_1}. \tag{9}$$

In our study the instantaneous overall Sherwood number was calculated in the following manner; the values of $\bar{Z}_1$, computed with equation (7), are interpolated with a taut cubic spline [20], and then equation (9) is applied to the resultant spline interpolant.

RESULTS

We restrict our investigation only to the case of a circulating droplet, so that in the Hadamard–Rybczynski velocity profile the viscosity ratio k is equal to one. The key parameters in the conjugate problem are the equilibrium constant H and the diffusivities ratio D_1/D_2. In this paper we consider only the situation when $H = 1.0$ and D_1/D_2 takes values from 0.01 to 100.0.

We split our search into two parts:

(i) We investigate the domain delimited by equal resistances of both phases and negligible external resistance; in all these situations we kept the internal Peclet number constant and equal to 100.0.

(ii) We explore the domain delimited by equal resistances of both phases and negligible internal resistance; in these situations we kept the external Peclet number constant and equal to 100.0.

Results with QIA are not presented because, a value of $Pe_1 = 100.0$ (our maximum value for the internal Peclet number) is too small to consider the Kronig–Brink mass transfer model adequate. In ref. [2] the criterion $Pe_1/(1+k) > 250.0$ is presented in order to accept that the mass transfer inside the droplet can be described by the Kronig–Brink model. Some preliminary tests made by the authors confirm these assumptions. For the same reason, too small values of *Pe*, the boundary layer theory is not applicable in our situation. The relative difference between the values of asymptotic Sherwood number at $D_1/D_2 = 1.0$ and $Pe_i = 100.0$ calculated with relations (48) and (55) of Chao [9] and with relation (9) is greater than 30%.

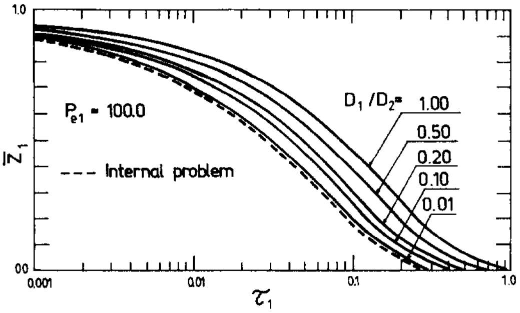

FIG. 1. Variation of average particle concentration with dimensionless particle time τ_1, for $D_1/D_2 \leqslant 1$.

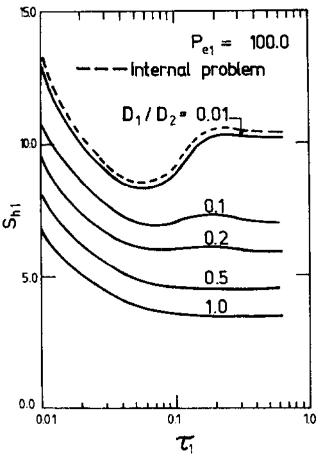

FIG. 2. Variation of instantaneous overall Sherwood number Sh_1 with dimensionless particle time τ_1, for $D_1/D_2 \leqslant 1$.

The time variation of the average particle concentration, $\bar{Z}_1$, and the instantaneous overall Sherwood number Sh_1, for the first situation are depicted in Figs. 1 and 2, respectively. It can be seen that the diffusivities ratio has a noticeable influence on both $\bar{Z}_1$ and Sh_1, and with the decrease of D_1/D_2 the curves approach the limiting case of the internal problem. In both figures the internal problem is depicted by a dashed line. At $D_1/D_2 = 0.01$ the maximum relative difference between the conjugate and internal solutions is about 5% for both $\bar{Z}_1$ (at $\bar{Z}_1 \geqslant 0.1$) and Sh_1. For $D_1/D_2 < 0.5$ the instantaneous Sh_1 exhibits small dumped oscillations, increasing with a decrease of the diffusivities ratio. Note also that at $D_1/D_2 = 1.0$ the agreement between our results and those depicted in ref. [1] is better than 1%.

Figure 3 shows the variation with τ_1 of $\bar{Z}_1$ for situation (ii). Like in the preceding situation D_1/D_2 has a noticeable influence on $\bar{Z}_1$. But from this figure it is hard to detect when the control of the dispersed phase becomes negligible. More information concerning the condition under which the internal resistance becomes negligible can be obtained if we depict $\bar{Z}_1$ as a function of τ_2 (Fig. 4), or if we depict together the $\bar{Z}_1$ and $\bar{Z}_s$ time variation (Fig. 5). $\bar{Z}_s$ is the average surface concentration calculated from

$$\bar{Z}_s = \frac{1}{2}\int_0^{\pi} Z\bigg|_{r=1} \sin\theta \, d\theta. \qquad (10)$$

To alleviate the agglomeration in Fig. 4 not all the curves presented in Fig. 3 are depicted. Figure 4 shows that at $D_1/D_2 \geqslant 10.0$ the resultant $\bar{Z}_1$ curves are very close to each other. The relative difference between the $D_1/D_2 = 25.0$, 50.0 and 100.0 solutions are approximately 1%. The dashed line in Fig. 4 represents the solution obtained with the 'quasi-steady external resistance approximation' [2] (QSERA). The QSERA curve converges to our solution at $D_1/D_2 = 100.0$ only for $\tau_2 > 0.1$. For smaller values of τ_2 significant discrepancies exist between our solution and QSERA. The explanation is that at $\tau_2 < 0.1$ the actual external instantaneous Sherwood number is much greater than the value which was used in the QSERA, the value of which corresponds to the steady-state value of the external problem for $Pe = 100.0$.

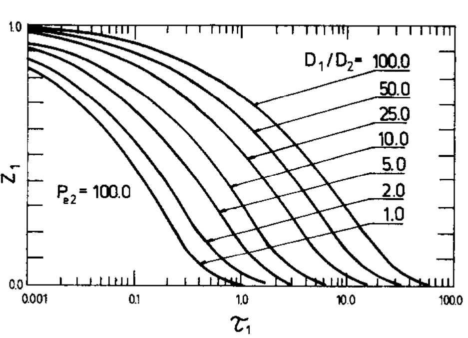

FIG. 3. Average particle concentration as a function of dimensionless particle time τ_1, for $D_1/D_2 \geqslant 1$.

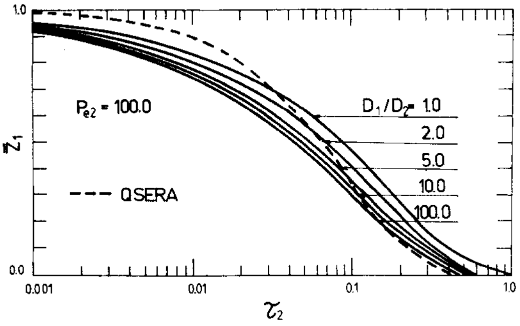

FIG. 4. Average particle concentration as a function of dimensionless time τ_2, for $D_1/D_2 \geqslant 1$.

Figure 5 shows that at short times there is a difference between $\bar{Z}_1$ and $\bar{Z}_s$. With the increase of the diffusivities ratio this difference diminishes. At long times the $\bar{Z}_1$ and $\bar{Z}_s$ curves converge. The convergence is faster at greater values of the diffusivities ratio.

The time variation of the instantaneous overall Sherwood number Sh_2 is drawn in Fig. 6. It can be seen that the influences of the diffusivities ratio on Sh_2 is more marked at values of D_1/D_2 comprised between 1.0 and 10.0. The dashed line represents the solution of the external problem. In this case, the difference between our solution at the extreme value of D_1/D_2 ($D_1/D_2 = 100.0$) and the limiting situation (external problem) is significant.

Asymptotic values of Sh_i for the first and second situation are presented in Table 1. As it is known from the literature [1, 10], the additivity formula

$$\frac{1}{Sh_i} = \frac{D_i}{D_1}\left(\frac{1}{Sh_{\mathrm{in}}} + \frac{D_1}{D_2}\frac{1}{Sh_{\mathrm{ex}}}\right) \qquad (11)$$

may be applied for the estimation of the asymptotic Sher-

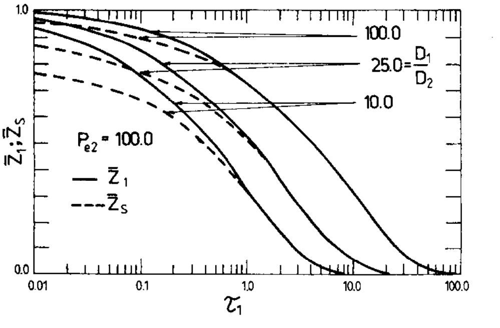

FIG. 5. Variation of average particle concentration and average surface concentration with dimensionless time τ_1, for $D_1/D_2 \geqslant 1$.

Table 1. Asymptotic values of Sherwood numbers

D_1/D_2	Pe_1	Pe_2	Sh_{in}	Sh_{ex}	Sh_i Equation (9)	Sh_i Equation (11)
0.01	100.0	1.0	10.8	2.72	10.5	10.40
0.1	100.0	10.0	10.8	3.45	7.1	8.25
0.2	100.0	20.0	10.8	4.14	6.0	7.07
0.5	100.0	50.0	10.8	5.45	4.5	5.43
1.0	100.0	100.0	10.8	6.9	3.5	4.21
2.0	50.0	100.0	8.2	6.9	4.1	4.86
5.0	20.0	100.0	6.9	6.9	4.7	5.75
10.0	10.0	100.0	6.75	6.9	5.1	6.27
100.0	1.0	100.0	6.71	6.9	5.6	6.83

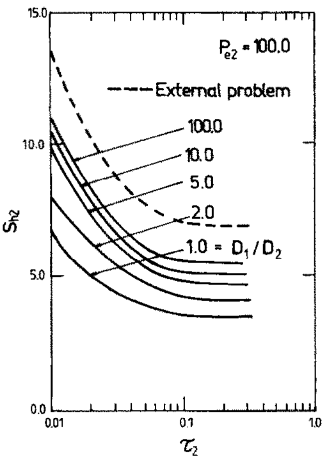

FIG. 6. Instantaneous overall Sherwood number Sh_2 as a function of dimensionless time τ_2, for $D_1/D_2 \geqslant 1$.

wood number. Table 1 shows that the additivity formula (11) is a rough estimation of the conjugate problem for $D_1/D_2 > 0.01$.

Finally we can conclude that our results confirm the assumptions used in ref. [2].

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