Prediction of mass transfer on a moving non oscillating spheroidal drop of clean water

B. Foudin, B. Caussade

INP - ENSEEIHT, Institut de Mécanique des Fluides de Toulouse, URA au CNRS, Avenue du Professeur Camille Soula, 31400 Toulouse, France

ABSTRACT

Numerical investigation of absorption into a moving spheroidal water drop (supposedly nonoscillating to simplify the problem) at terminal velocity using a finite difference method for Re=100-400 and aspect ratio (b/a) =0.70-0.97 is reported. The effect of deformation from spherical to spheroidal shape on mass transfer have been studied. The main conclusion is that any change in aspect ratio of the spheroid will cause an important variation on mass transfer rate; the more the oblateness of the drop becomes important, the more the transfer is enhanced.

INTRODUCTION

A better knowledge of gas absorption mechanisms by water drops is needed to understand scavenging of trace gases in clouds, rain and wet scrubbers. Our literature search has shown that theoretical approaches are inconclusive and that only the experimental study of Walcek et al. [11] has been carried out for testing the described theory of sulfur dioxide absorption and desorption into individual freely falling water drops. It is well known that a drop moving freely in a viscous fluid tends to deform from spherical to spheroidal shape in a large Reynolds number range, above all if the diameter is larger than 1mm. Masliyah and Epstein [10] have numerically studied the flow field around a rigid spheroid from low to intermediate Reynolds number range by a finite difference method. They extended their numerical analysis to the problem of heat transfer. Generally the deformation is accompanied by an oscillation of the shape of the drop, in relation to wake shedding, playing an important role in promoting mass transfer. For liquid drops in gases, oscillation has essentially no effect on transfer (as opposed to drops in liquids). So, to simplify the problem we consider a nonoscillating deformed circulating drop with fixed shape conveniently represented by a spheroid with semi-axis based on data given by Finlay [6], [7]. Firstly, we have developed a computational code to solve the transient hydrodynamics in the case of a drop of water accelerated from rest before considering the mass transfer problem, in respect to the aspect ratio E. The interest to solve the transport equation in conservative form is equally clearly shown.
NUMERICAL MODEL

Statement of the problem

The problem is to determine the rate of absorption and desorption of SO2 by a drop of water slightly deformed into an oblate spheroid, falling at its terminal velocity $U_\infty$ under the influence of gravity. The theoretical basis for modeling the transfer is the classical transport equation, which can be written in the following form:

$$\frac{\partial C}{\partial t} + \mathbf{U} \cdot \nabla C = \mathbf{D}_\mu \Delta C$$  \hspace{1cm} (1)

where $C$ is the concentration, $\mathbf{U}$ the velocity, $t$ the time and $\mathbf{D}_\mu$ the molecular diffusion.

In order to predict mass transfer in the case of trace gases, we have developed a model solving simultaneously the convective-diffusion equation (1) inside and outside the drop.

The choice of spheroidal coordinates in this study facilitates the formulation of the boundary conditions and the use of a finite difference method. In addition, the exponential properties of the coordinates give a fine lattice near the surface of the spheroid and especially near the tips, so as a coarse lattice far away from the interface.

Figure 1 shows the external oblate spheroidal mesh system near the interface, where $a$ and $b$, are the length of the major and minor semi-axis of the spheroid respectively, and determined from relationships (proposed by Chuchottawom [5] and others) established on the Eötvös number and experimental data given by Finlay [6].

Due to numerical and cost considerations, 2997 nodes inside and outside the drop have been utilized in our study.

The following assumptions have been used in this study:

i) the spheroidal circulating drop is accelerated under the influence of gravity,
ii) the molecular diffusivity $D_\mu$, viscosity $\nu$, and density $\rho$ are independent of the concentration,
iii) fluids are incompressible and newtonian,
iv) fluid motion and concentration distribution are axisymmetric,
v) no chemical reaction takes place except at the interface.
**Transient Flow Field**

For the circulation flow inside and outside the drop, the time dependent Navier-Stokes equations of motion can be written in oblate spheroidal coordinates \((\xi, \eta)\) with the Helmholtz formulation (stream function \(\psi\), and vorticity \(\omega\)). The following dimensionless quantities are used:

\[
\psi = \frac{\psi^*}{[U_p(t) a^2]} \quad \omega = \frac{\omega^*}{U_p(t)} \quad \Re(t) = 2 a U_p(t) / \nu_o \quad T = \mu_o t / [4 a^2 \rho_i]
\]

where \(\Re\) is the Reynolds number, \(U_p(t)\) is the particle velocity, \(t\) the time and the starred quantities are dimensional.

With axial symmetry, the vorticity vector \(\omega = V \times u\) is always in the azimuthal direction. The dimensionless radial and tangential velocity components are related to the stream function in spheroidal coordinates by:

\[
U_\xi = -\frac{\cosh^2 \xi^* \cosh \xi \sin \eta \sqrt{\cosh^2 \xi - \sin^2 \eta}}{\cosh \xi \sin \eta \sqrt{\cosh^2 \xi - \sin^2 \eta}} \frac{\partial \psi}{\partial \eta} \quad U_\eta = \frac{\cosh^2 \xi^* \cosh \xi \sin \eta \sqrt{\cosh^2 \xi - \sin^2 \eta}}{\cosh \xi \sin \eta \sqrt{\cosh^2 \xi - \sin^2 \eta}} \frac{\partial \psi}{\partial \xi}
\]

The equations satisfied by \(\psi\) and \(\omega\) are then as follows:

\[
E^2 \psi_x = \omega_x \cosh \xi \sin \eta \sech^3 \xi^*
\]

\[
\frac{\partial \omega_x}{\partial T} = 4 \cosh^2 \xi^* \left[ \frac{1}{\cosh^2 \xi - \sin^2 \eta} F^2 \omega_x - \frac{1+\cot^2 \eta}{\cosh^2 \xi} \omega_x \right] - \frac{2 \rho_i \Re(T) \cosh^3 \xi^*}{\rho_o \cosh \xi \sin \eta \left( \cosh^2 \xi - \sin^2 \eta \right)} G^2 \frac{\omega_x}{\Re(T)} \frac{d \Re(T)}{dT}
\]

with

\[
E^2 = \frac{1}{\cosh^2 \xi - \sin^2 \eta} \left( \frac{\partial^2}{\partial \xi^2} - \tanh \xi \frac{\partial}{\partial \xi} + \frac{\partial^2}{\partial \eta^2} - \cot \eta \frac{\partial}{\partial \eta} \right)
\]

\[
F^2 = \frac{\partial^2}{\partial \xi^2} + \frac{\partial^2}{\partial \eta^2} + \tanh \xi \frac{\partial}{\partial \xi} + \cot \eta \frac{\partial}{\partial \eta}
\]

\[
G^2 = \frac{\partial \psi_x}{\partial \xi} \frac{\partial}{\partial \eta} - \frac{\partial \psi_x}{\partial \eta} \frac{\partial}{\partial \xi} + \tanh \xi \frac{\partial \psi_x}{\partial \eta} - \cot \eta \frac{\partial \psi_x}{\partial \xi}
\]

\[
C = \frac{\mu_i}{\mu_o} \quad (x = i) \quad \text{or} \quad \frac{\rho_i}{\rho_o} \quad (x = o)
\]

where \(\xi_{a}\) is the value of \(\xi\) at the surface of the spheroid, \(\mu\) the dynamic viscosity, \(\nu\) the kinematic viscosity and \(x = \) subscripts \(i\) or \(o\) refer to inside or outside phase, respectively.

The boundary conditions to be satisfied are as follows:

i) far from the drop at the outer boundary: \(\xi = \xi_b\), undisturbed parallel flow is assumed:

\[
\omega_o = 0 \quad \psi_o = 1/2 \sin^2 \eta * \cosh^2 \xi_b * \sinh^{-2} \xi_a
\]

ii) along the axis of symmetry: \(\eta = 0, \pi\):

\[
\omega_i = 0 \quad \psi_i = 0 \quad \omega_o = 0 \quad \psi_o = 0
\]
iii) across the gas-liquid interface $\xi=\xi_d$, the following relations are taken into account, respectively:

**negligible material transfer:**
$$\psi_1 = 0, \quad \psi_0 = 0$$  \hspace{1cm} (6)

**continuity of tangential velocity:**
$$\frac{\partial \psi_1}{\partial \xi} = \frac{\partial \psi_0}{\partial \xi}$$  \hspace{1cm} (7)

**continuity of tangential stress:**
$$\frac{\mu_i}{\mu_o} \left( \frac{\partial^2 \psi_1}{\partial \xi^2} - \tanh \xi_a \frac{3 \cosh \xi_a \sin^2 \eta}{\cosh^2 \xi_a - \sin^2 \eta} \cdot \frac{\partial \psi_1}{\partial \xi} \right) = \frac{\mu_i}{\mu_o} \left( \frac{\partial^2 \psi_0}{\partial \xi^2} - \tanh \xi_a \frac{3 \cosh \xi_a \sin^2 \eta}{\cosh^2 \xi_a - \sin^2 \eta} \cdot \frac{\partial \psi_0}{\partial \xi} \right)$$  \hspace{1cm} (8)

Liquid and gas vorticity at the interface are given by:
$$\omega_l = \frac{\mu_o}{\mu_i} \left( \frac{\omega_0 - 2 \sinh \xi_a \cosh^3 \xi_a}{\sin \eta (\cosh^2 \xi_a - \sin^2 \eta)^2} \cdot \frac{\partial \psi_0}{\partial \xi} \right) + \frac{2 \sinh \xi_a \cosh^3 \xi_a}{\sin \eta (\cosh^2 \xi_a - \sin^2 \eta)^2} \cdot \frac{\partial \psi_1}{\partial \xi}$$
$$\omega_o = \frac{1}{\cosh \xi_a \sin \eta} \cdot \frac{\cosh \xi_a}{\sin \xi_a \cosh \xi_a \cos^2 \eta} \left( \frac{\partial^2 \psi_0}{\partial \xi^2} - \tanh \xi_a \cdot \frac{\partial \psi}{\partial \xi} \right)$$  \hspace{1cm} (9)

The solutions of the vorticity equations (3) need the particle velocity $U_p(t)$, which appears in the Reynolds number. For spheroidal drop accelerated under gravity (where added mass is neglected), the particle equation in nondimensional form is given by:

$$\frac{d \text{Re}}{dT} = \frac{8a^3 \cdot g(\rho_i - \rho_o) \cdot \rho_o}{\mu_o^2} - \frac{3}{4} \left( \frac{a}{r_e} \right)^3 \cdot C_d \cdot \text{Re}^2$$  \hspace{1cm} (10)

Here the drag coefficient is defined as: \( C_d = D / (1/2 \pi \cdot a^2 \cdot U_p(t)^2) \), \( g \) is the gravitational acceleration, \( \rho \) is the fluid density, \( D \) is the total drag force and \( r_e \) is the equivalent radii of a sphere of same volume.

**Mass Transfer**

In spheroidal coordinate and in nondimensional conservative form, equation (1) for mass transfer becomes:

$$\frac{\partial C_x}{\partial T} = - \frac{\cosh \xi_a \cdot P_e_x}{2 \cdot \cosh \xi \cdot \sin \eta (\cosh^2 \xi - \sin^2 \eta)} \left[ \frac{\partial (\cosh \xi \cdot \sin \eta \cdot (\cosh^2 \xi - \sin^2 \eta)^{1/2} \cdot U_{\xi_x} \cdot C_x)}{\partial \xi} + \frac{\partial (\cosh \xi \cdot \sin \eta \cdot (\cosh^2 \xi - \sin^2 \eta)^{1/2} \cdot U_{\eta_x} \cdot C_x)}{\partial \eta} \right]$$

$$+ \frac{\cosh \xi_a}{\cosh^2 \xi - \sin^2 \eta} \left[ \frac{\partial^2 C_x}{\partial \xi^2} + \frac{\partial^2 C_x}{\partial \eta^2} + \tanh \xi \cdot \frac{\partial C_x}{\partial \xi} + \cot \eta \cdot \frac{\partial C_x}{\partial \eta} \right]$$  \hspace{1cm} (11)
with dimensionless quantities:

$$C_x = C_x^* / (C_{\text{sat}} \text{or } C_{g^\infty}) \quad \text{Pe}_x = 2aU_\infty / D_x \quad T = D_xt / a^2$$

where $\text{Pe}_x$ is the Peclet number, $C_x$ is the liquid or gas concentration at a given location and time, $C_{\text{sat}}$ is the equilibrium liquid concentration, $C_{g^\infty}$ the gas concentration far away from the drop and the starred quantities dimensional. $T$ is the dimensionless time (different than in the hydrodynamic part), $U_x$ and $U_\eta$ the dimensionless radial and tangential velocities in the considered phase.

Boundary and initial conditions:

- the liquid is initially assumed to be clean:

$$T = 0 \quad 0 \leq \xi \leq \xi_a ; \quad 0 \leq \eta \leq \pi \quad C_l = 0$$

(12)

$$C_l = 1 \quad \xi_a \leq \xi \leq \xi_b ; \quad 0 \leq \eta \leq \pi$$

(13)

- very far from the drop, the gas concentration in the liquid phase is uniformly mixed:

$$T > 0 \quad \xi \geq \xi_b ; \quad 0 \leq \eta \leq \pi \quad C_g = 1$$

(14)

- along the axis and at the center of the drop, the flow concentration is axisymmetric:

$$T > 0 \quad 0 \leq \xi \leq \xi_b ; \quad \eta = 0, \pi \quad \partial C_l/\partial \eta = \partial C_g/\partial \eta = 0$$

(15)

- at the gas-liquid interface, mass flux continuity is imposed:

$$T > 0 \quad \xi \geq \xi_a ; \quad 0 \leq \eta \leq \pi \quad C_{\text{sat}}D_\eta \partial C_l/\partial \xi = \partial C_g/\partial \xi D_g C_{g^\infty}$$

(16)

- at the drop surface, a local saturated equilibrium exists between the liquid and the gas phases, then the equilibrium relation is given by:

$$C_{l_{\text{interface}}} = \left[ \frac{(K_1K_HC_{g^\infty})^{1/2}}{(K_1K_HC_{g^\infty})^{1/2} + K_HC_{g^\infty}} \right] \sqrt{C_{g_{\text{interface}}}} + \left[ \frac{K_HC_{g^\infty}}{(K_1K_HC_{g^\infty})^{1/2} + K_HC_{g^\infty}} \right] C_{g_{\text{interface}}}$$

(17)

where $C_{l_{\text{interface}}}, C_{g_{\text{interface}}}$ are the dimensionless concentrations in the liquid and the gas phases at the drop surface and $K_H$ and $K_1$ the equilibrium constants for dissolved SO$_2$ and dissociated H$_2$SO$_3$ in water (for more details, see Amokrane et al. [1,2]).

Here, we present results only for total sulfur $C = [\text{H}_2\text{SO}_3] + [\text{HSO}_3^-] + [\text{SO}_3^{2-}]$. The average concentration $<C>$ in the drop is calculated as a function of time from the following relation:

$$<C> = \int_0^\gamma C \cdot dv / \int_0^\gamma dv$$

(18)

where $\gamma$ is the total volume of the drop.
RESULTS

Figure 2 shows the calculated velocities vectors inside and outside an oblate water drop at its terminal velocity. The equivalent radii is about 420μm corresponding to a 3% oblateness i.e. an aspect ratio $E=b/a = 0.97$.

![Flow fields](image)

Figure 2: Internale (a) and external (b) flow fields in the case of an oblate drop at terminal velocity.

As we will see later, this flow fields has a large influence on the manner in which the gas is convected into the drop.

We have noticed that the interfacial dimensionless shear stress more important in the case of the deformed drop ($E=b/a=0.96$) but identical for the two shapes compared on and after the separation angle measured from front stagnation point.

Concerning the mass transfer problem, on plate 1 we present the numerical concentration fields for a 420μm spheroidal droplet as it falls at terminal velocity through a 2 ppm mixture of sulfure dioxide. These fields represent the numerical solutions of the full convective-diffusion equation inside and outside the drop.

![Concentration fields](image)

Plate 1: Numerical visualization of the concentrations fields for a $r_e=420μm$ spheroidal droplet at terminal velocity through a 2ppm mixture of sulfure dioxide.
First, we observe the influence of the internal circulation on the concentration profiles; the gas is carried in the rear of the drop and the angle of injection depends on the intensity of the secondary vortex. Streamlines and lines of constant concentration become coincident, and molecular diffusion carries SO\textsubscript{2} perpendicular to streamlines until the drop is in equilibrium with its environment. Correlatively to this increase of concentration in the rear part of the drop, we observe clearly a decrease of the external concentration in the wake of the drop in the interfacial region. Second, this plate shows an important gradient of concentration in the domain limited from 10 drop radii to the surface of the drop, after this concentration of the gas is uniform. This process, very important in the case of trace gases, confirms that the film theory concept outside the drop is unsatisfying (also see [8]). We observe that this wake rapidly disappears and the gas concentration becomes uniform up to the drop surface.

Figure 3 shows a comparison between our results and those found in literature. The hybrid model of Saboni [4], [3] (film theory outside the drop, transport equation inside the drop) largely overestimates the concentrations. This is not surprising because this model does not takes into account the external resistance to transfer observed at low gas concentration. Concerning the full model of Walcek [11] the discrepancies arrive from the velocity fields computed by Leclair (see Saboni).

The present work shows that the differences concerning the mean concentrations computed using a conservative or non conservative form of the transport equations are very weak. However, at 90° from the forward direction of the falling drop across the gas-liquid interface, we observe that the conservative or non conservative solutions are very different mainly inside the drop. The negative values which appear inside the drop, generated by the non conservative model, are instabilities of numerical type. In other words, the important positive and negative values near the interface in the liquid are smoothed in terms of mean concentration but, instantaneous maps of concentration clearly need a conservative form of transport equations.

The lack of experimental results in these zone restrain from concluding in favour of one of the models but, the MacCormack scheme [9] we have applied to solve the transport equation is particulary well adapted to this kind of problem and more, the drop deformation is taken in account, for this reason it seems logical to expect that our results are more accurate.

![Figure 3: Comparison between our results and numerical results from literature, as a function of the shape (r\textsubscript{e}=305\textmu m, C\textsubscript{g\infty}=10%).](image-url)
We note that the deformation seems to considerably increase the absorption rate. This is due to the strong convection created in the rear part of the drop. When the aspect ratio range from 0.9 to 0.7, the enhancement of mean concentration in the drop is of the order of 100%. Due to the fact that the presence of a surface active agent has not been taken into account in the mass transfer process, this study is essentially purely academic but shows that mass transfer rates could be largely affected by the oblateness of the drop.

CONCLUSIONS
The main conclusions of this numerical study are the following:
(i) the influence of the oblateness of the drop on mass transfer rates has been proved. The more the oblateness of the drop is important, the more the mass transfer is enhanced, this is particularly important in real atmospheric conditions in the presence of surface active agents.
(ii) in the case of trace gases it is necessary to solve the full transport model (inside and outside the drop) to take into account the external resistance to mass transfer due to the decrease of the concentration in the wake of the drop.
(iii) the solution of the transport equation in conservative form protect from numerical instabilities which can affect the instantaneous concentration fields.

Acknowledgements: The authors gratefully acknowledge the Région Midi-Pyrénées for providing funds for carrying out this research.

REFERENCES