MASS TRANSFER FROM A PULSATING DROP

V. P. Vorotilin and V. S. Krylov

Izv. AN SSSR. Mekhanika Zhidkosti i Gaza, Vol. 1, No. 6, pp. 100–105, 1966

The primary difficulty in solving the problem of mass transport through an isolated drop (or bubble) moving in a fluid medium at high Reynolds numbers lies in the extreme complexity of the hydrodynamic pattern of the phenomenon. For sufficiently high velocities a separation of the external flow will occur in the rear portion of the drops and bubbles, which leads to the appearance of a turbulent wake and a sharp increase of the hydrodynamic resistance. Beginning with those dimensions for which the resistance force acting per unit surface of the drop or bubble from the external medium becomes greater than the capillary pressure, the surface of the drops and bubbles begins to deform and pulsate. The local variations of the surface tension, resulting either from the process of convective diffusion or from adsorption of surface-active substances, have a large effect on the hydrodynamics of drops and bubbles (particularly on the deformation of their surface) [1, 2]. The presence of vertical, and possibly even turbulent, motion within the drops and bubbles may, under certain conditions [3], lead to their fractionation.

Naturally, at the present time such complex hydrodynamics cannot be described by exact quantitative relations. Several authors have attempted to solve this problem approximately within the framework of certain assumptions. In particular [3–5], a theory was developed for the boundary layer on the surface of spherical and ellipsoidal gaseous bubbles moving in a liquid. Studies were made of [7, 8] the hydrodynamics of drops located in a gas flow and the conditions for which fractionation of such drops takes place. Of considerable practical interest is the development of the theory of mass transfer in pulsating drops and bubbles and finding in explicit form the dependence of the mass transfer coefficients on the hydrodynamic characteristics of these systems. Until this relationship is established, every theory which ignores the effect of hydrodynamics on the mass transfer rate from an individual drop or bubble cannot be considered in any way well-founded. This relates particularly to the theories [9, 10] which consider mass transfer in systems with concentrated streams of drops and bubbles. The present paper is devoted to the study of mass transport through the surface of an isolated drop in an irrotational gas or liquid stream for large Peclet numbers P.

In the case of axisymmetric oscillations of a drop, the equation of its surface may be written [7] in the form of a series in Legendre polynomials \( P_n(\cos \phi) \), where \( \phi \) is the polar angle in a spherical coordinate system fixed at the center of the drop. The coefficients of this series are oscillating functions of the time \( t \). In the following we shall assume that the maximal oscillation amplitude \( a \) is small in comparison with the average drop radius \( R \), so that in the equation for the surface we may limit ourselves to only the first correction term

\[
r_s(\phi, t) = R \left[ 1 + \delta \cos \lambda t P_1(\cos \phi) \right],
\]

where \( \delta = a/R \ll 1 \).

Here \( \lambda \) is the pulsation fundamental frequency. We direct the polar axis in the direction of motion of the drop and we assume that the velocity field outside the drop is potential, while within the drop the velocity field has a vortex nature, in the zero approximation with respect to the parameter \( \delta \) described by the spherical vortex of Hill [11]. The fractionation conditions, derived under the assumption of the vortical nature of the velocity field within the drops [7], are in satisfactory agreement with the experimental data. The solution of the hydrodynamic equations leads, for the assumptions made, to the following velocity distribution:

- **a) within the drop**, \( v_x^{(i)} = U_0 \left[ \frac{3}{2} \left( 1 - \frac{v}{v_0} \right) + \delta \cos \lambda t \times \right. \)

\[
\left. \left[ - \frac{3}{5} \frac{\lambda R t g \lambda t}{U_0} P_1(v) + \frac{18}{5} \frac{\delta \xi^2}{v_0} P_2(v) \right] \right],
\]

- **b) outside the drop**, \( v_x^{(o)} = U_0 \left[ 1 - \frac{v}{v_0} \right] + \delta \cos \lambda t \times \)

\[
\left. \left[ - \frac{3}{5} \frac{\lambda R t g \lambda t}{U_0} P_1(v) + \frac{18}{5} \frac{\delta \xi^2}{v_0} P_2(v) \right] \right],
\]

Here \( U_0 \) is the drop velocity. The equations of convective diffusion in the internal (1) and external (2) phases, written in dimensional variables, have the form

\[
\frac{\partial c}{\partial \tau} + V_r^{(i)} \frac{\partial c}{\partial x} - \nabla^{(i)} \frac{\partial c}{\partial \tau} = \frac{1}{\rho} \Delta c, \quad (2)
\]

where \( \Delta c \) is the Laplace operator,

\[
\Delta c = \xi^2 \left[ \frac{\partial}{\partial \xi} \left( \xi^2 \frac{\partial}{\partial \xi} \right) + (1 - \nu^2) \frac{\partial^2}{\partial \nu^2} - 2\nu \frac{\partial}{\partial \nu} \right].
\]

Let us consider the case in which the mass transfer is limited by the resistance of the external phase. In this case the value of the concentration \( c_0 \) on the surface of the drop is the same at all points and depends only on the time. Considering a time in the course of which the total amount of matter dissolved in the drop cannot change appreciably, we can consider the value of \( c_0 \) constant in time. We shall denote the concentration of matter far from the drop (as \( \xi \to \infty \)) by \( c_1 \). For small values of the parameter \( \varepsilon = 1/\left( P^2 \right)^1/2 \) Eq. (2) may be solved by the method of the modified Poincaré-Lighthill-Kuo disturbance theory [12].

For this we convert from the independent variables \( \xi, \nu, \tau \) to the independent variables \( \rho, \nu, \tau \), where \( \rho \)
is determined by the relation
\[ \xi = 1 + \varepsilon \rho + \delta \cos \lambda \mu \rho \]

Representing the sought distribution \( c(\rho, \nu, \tau) \) in the form of the expansion
\[ c = c^{(0)} + \varepsilon c^{(1)} + \delta c^{(0)} + \ldots \]
we obtain for the function \( c^{(0)} \) the boundary-value problem
\[ \frac{\partial c^{(0)}}{\partial \tau} - 3\rho \frac{\partial c^{(0)}}{\partial \rho} - \frac{3}{2} (1 - \nu^2) \frac{\partial c^{(0)}}{\partial \gamma} + \frac{\partial c^{(0)}}{\partial \gamma^2} = 0, \]
\[ c^{(0)}(\rho, \nu, 0) = c_1, \quad c^{(0)}(\infty, \nu, \tau) = c_1, \quad c^{(0)}(0, \nu, \tau) = c_0. \tag{3} \]

The solution of this equation determines the right sides of the equations for the functions \( c^{(1)} \) and \( c^{(2)} \):
\[ \frac{\partial c^{(1)}}{\partial \tau} - 3\rho \frac{\partial c^{(1)}}{\partial \rho} - \frac{3}{2} (1 - \nu^2) \frac{\partial c^{(1)}}{\partial \gamma} + \frac{\partial c^{(1)}}{\partial \gamma^2} = 0, \]
\[ \frac{\partial c^{(2)}}{\partial \tau} - 3\rho \frac{\partial c^{(2)}}{\partial \rho} - \frac{3}{2} (1 - \nu^2) \frac{\partial c^{(2)}}{\partial \gamma} + \frac{\partial c^{(2)}}{\partial \gamma^2} = 0. \tag{4} \]

The solutions of (4) and (5) must satisfy the zero initial and boundary conditions. To find the function \( c^{(0)}(\rho, \nu, \tau) \) we convert in Eq. (3) from the variables \( \rho, \nu, \tau \) to the variables \( r, \gamma, \tau \), where \( r \) and \( \gamma \) are determined by the relations
\[ r = \frac{2}{3} \rho (1 - \nu^2), \]
\[ \gamma = \frac{3}{2} (1 - x^2) dx = \frac{1}{2} (2 + \nu) (1 - \nu^2). \tag{6} \]

In these variables, (3) takes the form
\[ \frac{\partial c^{(0)}}{\partial \tau} + \frac{9}{4} (1 - \nu^2) \left( \frac{\partial c^{(0)}}{\partial \gamma} - \frac{\partial c^{(0)}}{\partial \gamma^2} \right) = 0. \tag{7} \]

We apply the integral Laplace transformation to (7) and introduce the functions \( C_p^{(0)}(\psi, \xi, \tau) \), related with the Laplace transform \( c^{(0)}(\rho, \nu, \tau) \) of the sought function \( c^{(0)}(\psi, \xi, \tau) \) by the relation
\[ C_p^{(0)}(\psi, \xi, \tau) = \left( \frac{1 - \nu \psi^2}{1 + \psi} \right) c^{(0)}(\psi, \xi, \tau) - \frac{\psi_1}{p}. \tag{8} \]

Then for the function \( C_p^{(0)}(\psi, \xi, \tau) \) we obtain the equation
\[ \frac{\partial C_p^{(0)}}{\partial \tau} = \frac{\partial C_p^{(0)}}{\partial \xi}, \tag{9} \]
with the boundary conditions
\[ C_p^{(0)}(0, \xi, \tau) = 0, \]
\[ C_p^{(0)}(\infty, \xi, \tau) = \frac{1 - \nu \psi^2}{1 + \psi} (c_0 - c_1), \]
\[ C_p^{(0)}(\psi, \infty, \tau) = 0. \]

The solution of this equation has the form
\[ C_p^{(0)}(\psi, \xi, \tau) = \frac{2}{3} (c_0 - c_1) \times \]
\[ \int_{\xi}^{\infty} \frac{\operatorname{erf} \left( \frac{\psi - \nu(y)}{2 \sqrt{1 - \nu \psi^2}} \right) \left[ 1 - \nu(y) \right]^{3/2} \left[ 1 - \nu(y) \right]^{3/2}}{\left[ 1 - \nu(y) \right]^{3/2}} dy, \]

where \( \nu(y) \) is determined by the relation \( y = (2 + \nu) (1 - \nu^2)/2 \). Substituting this solution into Eq. (8) and performing the inverse Laplace transformation, we find, with account for (6),
\[ c^{(0)}(\rho, \nu, \tau) = c_0 - (c_0 - c_1) \times \]
\[ \int_{\xi}^{\infty} \frac{\operatorname{erf} \left( \frac{\psi - \nu(y)}{2 \sqrt{1 - \nu \psi^2}} \right) \left[ 1 - \nu(y) \right]^{3/2} \left[ 1 - \nu(y) \right]^{3/2}}{\left[ 1 - \nu(y) \right]^{3/2}} dy, \]

where \( \eta(v, \tau) = (1 + \nu) (1 + \nu^2) \exp(-2 \tau) \).

In the following we shall limit ourselves to finding the correction \( c^{(2)} \) due to the non spherical form of the drop. It is evident that this correction will play the primary role (in comparison with \( c^{(1)} \)) in satisfying the condition \( \varepsilon << \delta \), i.e., for very large values of the Peclet number in the external phase. Equation (5), written in the variables \( \psi, \xi, \tau \), has the form
\[ \frac{\partial c^{(2)}}{\partial \tau} + \frac{9}{4} (1 - \nu^2) \left( \frac{\partial c^{(2)}}{\partial \xi} - \frac{\partial c^{(2)}}{\partial \xi^2} \right) = 0. \tag{12} \]

where
\[ F(\psi, \xi, \tau) = \frac{\psi}{\sqrt{\xi - \chi(\nu, \tau)}} \times \left[ 2\nu^2 - \frac{3 (1 - \nu^2) - (1 - \eta \xi^2)}{\xi - \chi(\nu, \tau)} \right] \times \]
\[ \frac{A_1(\nu, \tau) - A_1(\nu, \tau)}{A_1(\nu, \tau) - A_1(\nu, \tau)} \exp \left( -\frac{\psi^2}{4 \xi - \chi(\nu, \tau)} \right), \]
\[ \chi(\nu, \tau) = \frac{3}{2} [2 + \eta(v, \tau)] \left[ 1 - \eta(v, \tau) \right]^2, \]
\[ A_1(\nu, \tau) = \frac{3}{2} (15 \nu^2 - 1) \cos \lambda_1 \tau - \nu \lambda_1 \sin \lambda_1 \tau, \tag{13} \]
\[ A_2(\nu, \tau) = \frac{3}{2} (30 \nu^2 - 23) \cos \lambda_1 \tau - 2 (3 \nu - 1) \lambda_1 \sin \lambda_1 \tau. \tag{14} \]

Solving (12) with account for the zero initial and boundary conditions by the method of the Laplace transformation with subsequent replacement of the sought transformant \( c_p^{(2)}(\psi, \xi, \tau) \) by the function \( [(1 - \nu^2)/(1 + \nu)]^{p/3} c_p^{(0)}(\psi, \xi, \tau) \), we find
\[ c_p^{(2)}(\psi, \xi, \tau) = \frac{2}{9\nu^2} \int_{\xi}^{\infty} \int_{\xi}^{\infty} F_p(\xi, y, \mu) \times \]
\[ \left[ \left( 1 + \nu \right) \left( 1 + \nu \right) \right]^{3/2} \left[ 1 - \nu \psi^2 \right] \left[ 1 - \nu \psi^2 \right] \times \]
\[ \left[ 1 - \nu \psi^2 \right] \left[ 1 - \nu \psi^2 \right] \times \left[ \frac{\psi - \nu(y)}{2 \sqrt{1 - \nu \psi^2}} \right] \times \]
\[ \frac{\operatorname{erf} \left( \frac{\psi - \nu(y)}{2 \sqrt{1 - \nu \psi^2}} \right) \left[ 1 - \nu(y) \right]^{3/2} \left[ 1 - \nu(y) \right]^{3/2}}{\left[ 1 - \nu(y) \right]^{3/2}} dy, \]

where \( F_p(x, y, \psi) \) is the Laplace transformant of the function \( F(x, y, \tau) \), and the relationships \( \nu(\xi) \) and \( \nu(\nu) \) are determined by the second of relations (6). With an accuracy to terms of first order in the asphericity