PREDICTION OF INTERFACIAL MASS TRANSFER IN LIQUID-LIQUID SYSTEMS WITH MOVING INTERFACES

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A numerical methodis developed that allows mass transfer at moving interfaces to be rigorously captured. The advantage of this method is its ability to consider arbitrary-form boundary conditions at the phase interface. The method is applied to the test system comprising the movement of a rising toluene droplet in a quiescence aqueous phase, with acetone being the transferring component. The level set method is employed for the description of the droplet movement, whereas the velocity and concentration fields are determined from the continuity, momentum and mass transfer equations. The concentration contours obtained are found to be in qualitative agreement with the available data from the literature.

1. INTRODUCTION

Liquid-liquid extraction processes are often based on the interaction of droplets moving in a continuous phase. The process performance depends on both the droplet movement and mass transfer between the droplets and continuous liquid phase.Both phenomena are interrelated, and their rigorous description requires solution of a coupled problem including momentum and mass transport at and around moving interfaces. Such problems are very difficult, since the deformation of the interface influences interfacial mass transfer and vice versa, so that the traditional assumption that the velocity field is not affected by the concentration field cannot be made.

In such cases, front capturing methods, e.g. volume of fluid (VOF) and level set (LS) methods, have proven to be useful (Bothe et al., 2003; Yang and Mao, 2005; Haroun et al., 2010). These methods are based on using an indicator function which is described by an advection equation. The latter has to be solved simultaneously with both momentum and mass transfer equations, because, generally, the deformation of the interface depends on mass transfer.

Handling of boundary conditions at the moving interface makes numerical solution of such problems particularly tricky. The common assumption of the thermodynamic equilibrium at the interface brings about a concentration jump which is numerically demanding and difficult to implement into the front capturing methods (Bothe et al., 2003). In addition, the component flux continuity at interface should also be fulfilled at the interface.

In this paper, we suggest a new approach to the solution of problems with moving interfaces, which can handle arbitrary-form interfacial concentration jump conditions and is not limited by a single and constant distribution coefficient. The new approach is illustrated with a test case study in which a toluene droplet rising in water is considered, with acetone as the transferred component.

2. THEORY

Both the droplet phase (denoted by d) and the continuous phase (denoted by c) are considered as binary mixtures. The governing system of equations consists of the continuity and momentum equations for incompressible flow and the binary mass transfer equation. These equations read as follows:

$$\nabla \cdot \vec{u} = 0 \tag{1}$$

$$\rho \frac{\partial \vec{u}}{\partial t} + \rho \left(\vec{u} \cdot \nabla \right) \vec{u} = -\nabla p + \rho \vec{g} + \nabla \cdot \mu \left[\nabla \vec{u} + \left(\nabla \vec{u} \right)^T \right] + \vec{F}_\sigma \tag{2}$$

$$\frac{\partial C}{\partial t} + \vec{u} \cdot \nabla C = \nabla \cdot \left(D \nabla C \right) \tag{3}$$

Eqs. (1)-(3) are valid for both contacting phases. The governing equation for the interface movement is given by

$$\frac{\partial f_{LS}}{\partial t} + \nabla \cdot \left(\vec{u} f_{LS} \right) = 0 \tag{4}$$

Here the standard LS function is defined as a distance function, i.e.

$$\left| f_{LS} \left(\vec{x} \right) \right| = \min_{x_I \in I} \left(\left| \vec{x} - \vec{x}_I \right| \right) \tag{5}$$

where I is the interface, $f_{LS}\left(\vec{x} \right) > 0$ at one side of the interface and $f_{LS}\left(\vec{x} \right) < 0$ at another side of the interface.

The equation system given above requires a numerical solution. The latter largely depends on the discretisation method and the treatment of the discretised computational domain. To achieve numerical robustness, the moving interface is artificially smeared out using the following regularised Heaviside function (Olsson and Kreiss, 2005):

$$H_\varepsilon \left(f_{LS} \left(\vec{x} \right) \right) = \begin{cases} 0, & \text{if } f_{LS}\left(\vec{x} \right) < -\varepsilon, \\ \frac{1}{2} \left(1 + \frac{f_{LS}\left(\vec{x} \right)}{\varepsilon} + sin\left(\pi f_{LS}\left(\vec{x} \right) / \varepsilon \right) / \pi \right), & \text{if } \left| f_{LS}\left(\vec{x} \right) \right| \le \varepsilon, \\ 1, & \text{if } f_{LS}\left(\vec{x} \right) > \varepsilon, \end{cases} \tag{6}$$

where ε is a numerical parameter equal to a half of the thickness of the "smeared-out" interface.

Olsson and Kreiss (2005) suggested using the regularised Heaviside function (Eq. (6)) as a LS function in order to overcome the mass loss drawbacks of the classical LS method:

$$\phi = H_\varepsilon \left(f_{LS} \left(\vec{x} \right) \right) \tag{7}$$

By this formulation,it is possible to localise the interface smeared out over a small distance equal to 2ε. The function defined by Eq. (7) takes the value of 0.5 exactly at the interface and the values 0 or 1 away from the interface.

The interface movement is capturedusing the following advection equation (Olsson et al., 2007):

$$\frac{\partial \phi}{\partial t} + \nabla \cdot \left(\phi \vec{u} \right) = \gamma \nabla \left(-\phi \left(1 - \phi \right) \frac{\nabla \phi}{|\nabla \phi|} + \varepsilon \nabla \phi \right) \tag{8}$$

where$t$ is time, $\vec{u}$ is velocity, γ is a re-initialization factor that should take values in the range of the maximum velocities, ε is a numerical parameter equal to a half of the thickness of the smeared-out interface. The re-initialization factor is used to maintain the thickness of smeared out interface constant. This is necessary since the movement of the interface causes changes of the ϕ function and thus, the interface thickness does not remain constant.

Both liquid phases have different densities and viscosities; therefore, a smooth variation of both these quantities across the interface is introduced as follows:

$$\rho = \rho_c + \left(\rho_d - \rho_c \right) \phi \tag{9}$$

$$\eta = \eta_c + \left(\eta_d - \eta_c \right) \phi \tag{10}$$

The surface tension description is based on the continuum surface force model proposed by Brackbill et al. (1992). In this model, the surface tension force is represented as a volume force:

$$\vec{F}_\sigma = \left(\sigma \kappa \vec{n} \right) |\nabla \phi| \tag{11}$$

The normal vector $\vec{n}$ and curvature κ at the fluid-fluid interface are determined in terms of the level set function:

$$\vec{n} = \frac{\nabla \phi}{|\nabla \phi|}\bigg|_{\phi=0.5} \tag{12}$$

$$\kappa = -\nabla \cdot \vec{n} \tag{13}$$

For the mass transport equations, two interfacial boundary conditions have to be fulfilled. First, the interfacial concentration jump is defined by the thermodynamic equilibrium assumption:

$$C_d = H_D C_c \tag{14}$$

where C is molar concentration, H_D is distribution coefficient.

Second, the interfacial fluxes obey the continuity condition:

$$D_c \frac{\partial C_c}{\partial n} = D_d \frac{\partial C_d}{\partial n} \tag{15}$$

where D_c and D_d are binary diffusivities of continuous and dispersed phase, respectively. The no-slip boundary condition is set at the wall boundaries.

3. NEW APPROACH

In this work, we suggest a general approach capable of handling mass transfer problems with moving interfaces. Its main idea is to incorporate the interfacial boundary conditions (e.g., Eqs. (14),(15)) into the mass transfer equations. It has to be done in such a way that the boundary conditions are fulfilled only in the region very close to the interface, whereas, outside this region, the initial mass transfer equations are valid. More exactly, the interfacial mass transfer related boundary condition is directly implemented into the mass transfer equations as an additional source term. For the boundary conditions given by Eqs. (14),(15), the following extended equations are obtained:

$$\frac{\partial C_d}{\partial t} + \vec{u} \cdot \nabla C_d = \nabla \cdot \left(D_d \nabla C_d \right) + \alpha_1 \left(D_c \frac{\partial C_c}{\partial n} - D_d \frac{\partial C_d}{\partial n} \right) \tag{16}$$

$$\frac{\partial C_c}{\partial t} + \vec{u} \cdot \nabla C_c = \nabla \cdot \left(D_c \nabla C_c \right) + \alpha_2 \left(C_c - \frac{C_d}{H_D} \right) \tag{17}$$

Here α_1 and α_2 represent parameters whose values at the interfaceare set sufficiently high (e.g., 10^5), so that the boundary conditions are fulfilled only there. In the rest of the computational domain, α_1 and α_2 are equal to zero, thus transforming Eqs. (16),(17) into the original mass transfer equations.As we have two interfacial boundary conditions to be fulfilled, mass transfer equation should be solved for each phase for the major part of the whole computational domain.

The suggested method can be used for any fluid-fluid systems and permits H_D to vary throughout the computational domain. Furthermore, the method is not limited to systems with binary mass transfer; it can readily be extended to multicomponent systems.

4. IMPLEMENTATION

In this work, a 2D implementation is applied and the governing equations (continuity, momentum, LS and extended mass transfer equations)are solved simultaneously, usingthe commercial finite-element-based solver COMSOL Multiphysics 3.5a. The minimum time step value of 0.0001s was used.The solver uses an affine invariant form of the damped Newton method as described in (Argyris et al., 1997). The convergence criterion is based on a weighted Euclidean norm of the estimated relative error (COMSOL AB, 2008). The iterations are terminated when the relative tolerance 0.0001exceeds the relative error with respect to all variables, viz. pressure, velocity, LS function and concentration.

4.1 Geometry and mesh

A non-uniform grid with triangular elements is selected.The circumference of the droplet is subdivided onto 128 mesh elements (each triangular element is 50 μm large).The mesh in the region occupied by the continuous phase above the droplet must be very fine, in order to capture the droplet movement properly (cf. Fig. 1a).A small domain (10mm x 12mm) is selected. The mass transfer process is much slower than the droplet rising within the domain. For this reason, the simulation is interrupted when the droplet approaches the upper boundary of the computational domain. Afterwards, the domain is moved upwards by 5mm and reinitialised. The velocity and concentration fields in the overlapping part of the two domains, (shown in Fig. 1b), are used as new initial conditions to initialise the second simulation step. The simulations are carried out during 500ms.
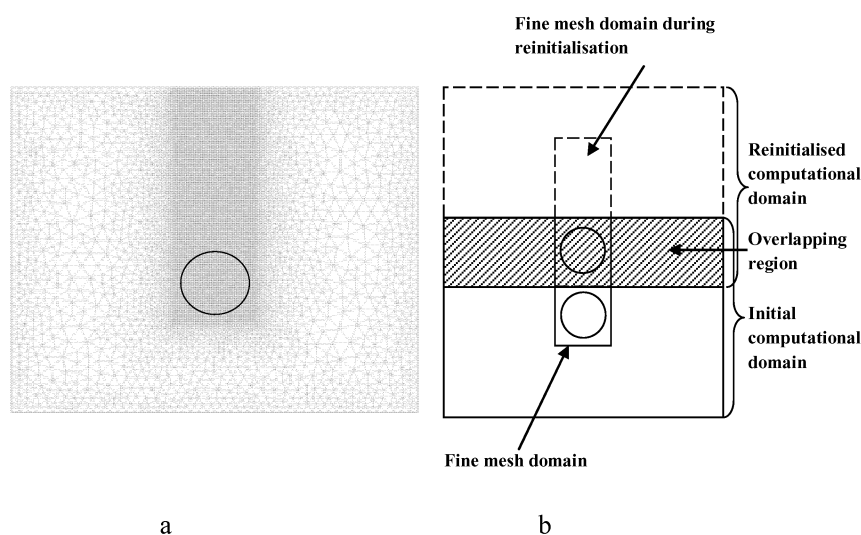
Fine mesh domain during reinitialisation

Reinitialised computational domain

Overlapping region

Initial computational domain

Fine mesh domain

a   b

Fig. 1: Computational domain and grid (a); illustration to the reinitialisation of the computational domain (b)

4.2 Boundary conditions

The no-slip boundary condition is used at the walls. The boundary of the droplet is in essence the interface between the two liquid phases; initially it has a circular form. LS value of 0.5 is allocated to all points of the circular interface, whereas the LS values of zero and one are assigned to both sides of the interface. However, the smooth variation of the LS function has to be performed during the initialisation step.

4.3 Solution procedure

The physical properties (density ρ, viscosity μ, surface tension σ and diffusivity D), the concentration C in each phase and ϕ as the distance function are set.The LS function is initialised. It should vary smoothly across the interface from zero to one. To obtain ϕ, Eq. (8) (here without term $\nabla \cdot (\phi \vec{u})$, as $\vec{u} = 0$) is solved until $t \approx 5\varepsilon/\sigma$. As the initial condition for ϕ, two pre-set values (zero and one) are used atdifferent sides of the interface.The continuity and momentum equations are solved iterativelyalong withEq. (8), (16) and (17), in such a way that the horizontal and vertical velocity components are delivered as an input to the mass transfer equations. The interfacial boundary condition, Eq. (14) and (15), should be fulfilled in a region very close to the interface. Test simulations were performed with varying ϕ limits, and it was found that the simulations for $0.4 \leq \phi \leq 0.6$ yeilded stable results. Therefore, the region $0.4 \leq \phi \leq 0.6$ is chosen for all simulations in this work.

5. RESULTS AND DISCUSSION

A toluene droplet with diameter 2mm rising in quiescent aqueous phase is considered. The concentration of acetone in the toluene droplet is 0.01kg/m^3. At this concentration, the surface tension has no effect on mass transfer from dispersed to continuous phase (Wegener et al., 2009a).Numerical simulations are carried out till $t = 500$ ms. For the present simulations, different values of α_1 and α_2 were tested ($10^4 \leq \alpha_1, \alpha_2 \leq 10^7$)and the value $10^5$was found to give the best results. This study was performed for the lower concentration of acetone in

dispersed phase (0.01 kg/m^3) to exclude the Marangoni convection onset typical at higher concentrations (Wegener et al. 2009b). Similar values of α_1, α_2 have recently been tested for gas-liquid systems (oxygen-water systems) yielding reasonably good results (Ganguli and Kenig, 2011).

The concentration contours at different time instants during the droplet rise are shown in Fig. 2. The decrease in acetone concentration inside the droplet can be observed. It starts from the centre (Fig. 2a). An interplay of the convective flow and diffusion in the continuous phase brings about a streak of acetone directed downwards from the droplet bottom (Fig. 2b-2d).These results are similar to the experimental observations of Kück et al., (2009).
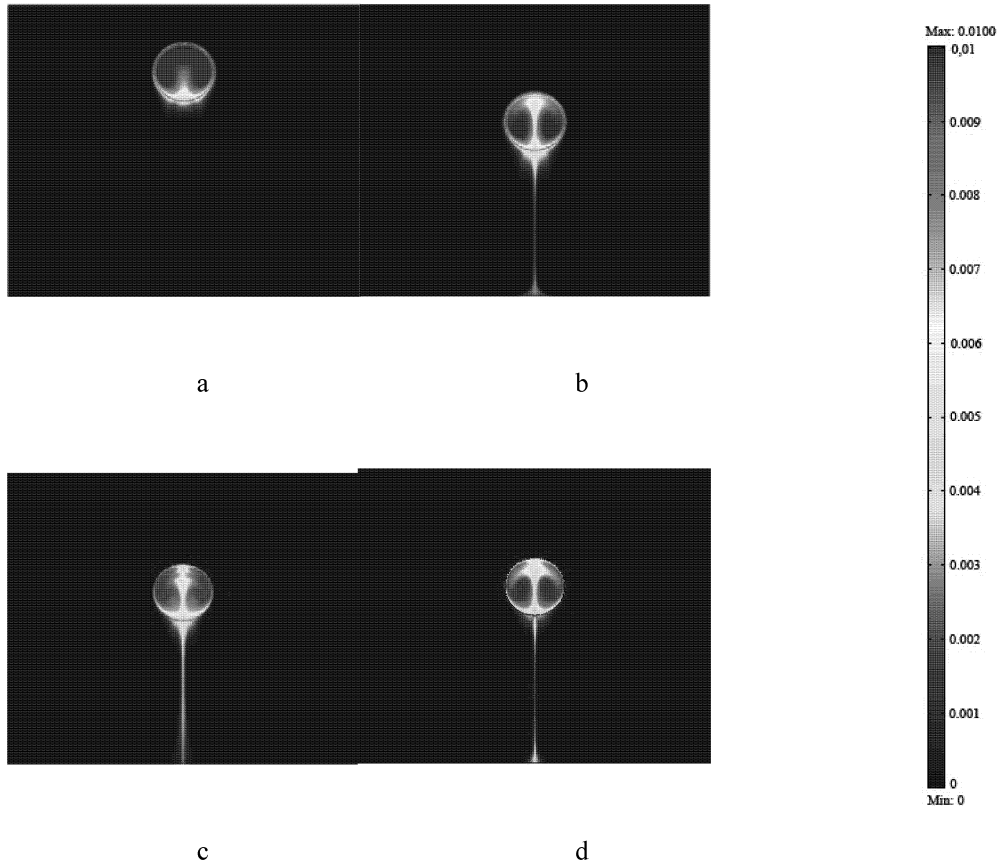

Fig.2: Concentration contours of acetone (gram/litre)*: t=120ms (a); t=275ms (b); t=400ms (c); t=500ms (d)*

6. CONCLUSIONS

In this work, a method is suggested that enables the rigorous treatment of coupled mass transport boundary conditions (thermodynamic equilibrium, flux continuity) at the moving liquid-liquid interface. With respect to the mass transfer related interfacial boundary conditions, the method has hardly any limitation, since the expressions in the source terms can be given in an arbitrary way. Thus, it can readily be extended to cover multicomponent systems and different fluid-fluid process conditions. The method is implemented into COMSOL Multiphysics 3.5a and tested for a system comprising rising toluene droplet in a continuous aqueous phase, with the mass transfer of acetone between them. A good qualitative agreement with the results from literatureis established. In the subsequent work, the capacity and robustness of the new method will further be tested.

7. REFERENCES

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