

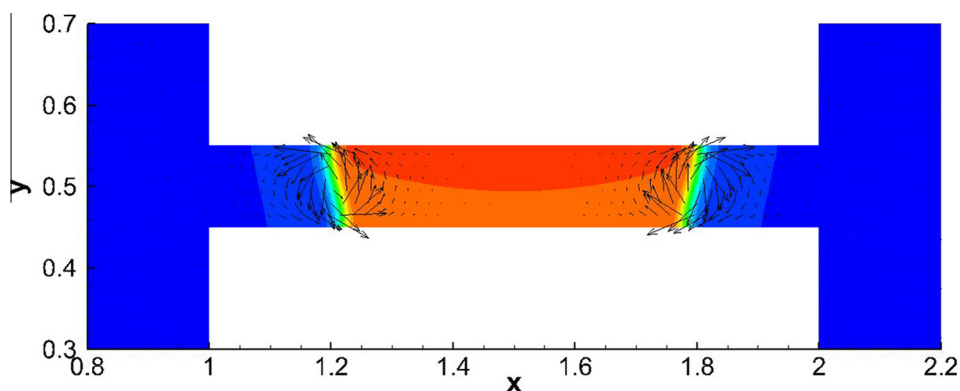
# On the phase-field modelling of a miscible liquid/liquid boundary



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## GRAPHICAL ABSTRACT



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## ABSTRACT

Mixing of miscible liquids is essential for numerous processes in industry and nature. Mixing, i.e. interpenetration of molecules through the liquid/liquid boundary, occurs via interfacial diffusion. Mixing can also involve externally or internally driven hydrodynamic flows, and can lead to deformation or disintegration of the liquid/liquid boundary. At the moment, the mixing dynamics remains poorly understood. The classical Fick's law, generally accepted for description of the diffusion process, does not explain the experimental observations, in particular, the recent experiments with dissolution of a liquid solute by a liquid solvent within a horizontal capillary (Stevan and Vorobev, 2012). We present the results of the numerical study aimed at development of an advanced model for the dissolution dynamics of liquid/liquid binary mixtures. The model is based on the phase-field (Cahn–Hilliard) approach that is used as a physics-based model for the thermo- and hydrodynamic evolution of binary mixtures. Within this approach, the diffusion flux is defined through the gradient of chemical potential, and, in particular, includes the effect of barodiffusion. The dynamic interfacial stresses at the miscible interface are also taken into account. The simulations showed that such an approach can accurately reproduce the shape of the solute/solvent boundary, and some aspects of the diffusion dynamics. Nevertheless, all experimentally-observed features of the diffusion motion of the solute/solvent boundary, were not reproduced.

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## 1. Introduction

It is known that the rate of diffusion of weak impurities in liquids is well defined by the classical Fick's law, i.e. with the gradient flux linearly proportion to the gradient of concentration. It is also

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known that this simple approach is not valid for the case of large concentration gradients, in particular, for the description of diffusion at a liquid/liquid (solute/solvent) boundary. This, in particular, was illustrated by the recent experiments, where mixing of liquid solute and liquid solvent was investigated [1]. The settings of the experiments were rather simple: a long capillary, initially saturated with one liquid (solute), was immersed horizontally into a solvent-filled thermostatic bath. The tube's diameters varied from 0.2 mm to 1.6 mm. Both ends of the tube were open, and no pressure gradients between the tube ends were applied. The experiments were conducted with different liquids, in particular, with the glycerol/water and soybean oil/hexane binary mixtures which are miscible in any proportions. Following the common expectations one would assume that the solute/solvent boundaries should remain stationary (if there are no mechanisms for the hydrodynamic flows) and would just slowly smear in time. Contrary to this, two solute/solvent boundaries were seen at the sides of the capillary for very long time periods. The interfaces were moving towards the middle of the tube with the speed that was considerably higher than the rate of interface smearing. The speed of the interface movement depended on time as  $t^{-1/3}$  in the beginning and  $t^{-2/3}$  in the later moments. In addition, it was observed that the interface should be endowed with the surface tension, since its inclined shape should be described by the balance of the capillary and gravity forces. The rate of interface propagation was found to depend on the tube's diameter, so the dissolution occurred slower in the tubes of smaller diameters. The speed of the interface movement did not depend on the shape of the tube's cross section and on the tube's length. The convective flows were found negligible, and thus the evolution of the interfaces was suggested to be primarily diffusion-driven.

In the current work, we aim to develop a theoretical model capable of reproducing this behaviour. We start with the use of the classical Fick's law with however the diffusion coefficient that strongly depends on concentration. Strictly speaking, this approach does not distinguish the phases, but the concentration dependence of the diffusion coefficient permits modelling of sharper diffusion fronts. After that, we introduce the concept of interface by adopting the phase-field approach.

Currently, the phase-field approach is mostly used as a numerical tool for tracing immiscible interfaces [2–5]. In the current work, however, this approach is used as a comprehensive physical model capable of describing the thermo- and hydrodynamic evolution of multiphase binary mixtures with undergoing phase transformations. Within the phase-field model, the diffusion process is defined through the gradient of the chemical potential, taking into account the effect of barodiffusion [6,7]. This model also captures the surface tension effects existent at miscible boundaries, thus permitting us to model the inclined shape of the solute/solvent boundary. Finally, we also add the hydrodynamics to investigate its possible role in the mixing of two liquids confined into a capillary.

The importance of the surface tension effects for miscible interfaces was first emphasized by Korteweg and van der Waals, who suggested that these effects can be mimicked by gradients of concentration [8]. Cahn and Hilliard [9,10] proposed to define the free energy as a function of not only concentration but also of the concentration gradient, adding a term that takes into account the surface tension effects. They used this approach primarily to model the dynamics of phase transitions in solids [11,4]. Later, the same idea was used to define the phase transitions in liquids, and the full equations for the thermo- and hydrodynamic evolution of liquid/liquid binary mixtures were derived by Lowengrub and Truskinovsky [12]. The resultant Cahn–Hilliard–Navier–Stokes equations were hardly feasible for the numerical treatment mostly

due to the necessity to use the full continuity equation because the mixture density is in general a function of concentration. Later, on the basis of the multiple-scale method, the quasi-acoustic effects were filtered out, so the Boussinesq approximation of the full equations was obtained [6].

Some features of the Cahn–Hilliard–Navier–Stokes equations were earlier used in different numerical studies. For instance, a model that takes into account the Korteweg force but assumes that diffusion is still driven by the simple Fick's law was used to simulate the miscible displacement of one liquid by another from a capillary [13–15]. The consideration was however limited for a rather fast process at very high Peclet numbers, when the effect of diffusion was negligible. The similar approach was used to study the spreading of the interface boundary and generation of the convective motion near the boundary by the action of the Korteweg force [16,17].

The evolution of a miscible droplet immersed into another liquid that is enclosed into capillary and subjected to axial rotation (the configuration of the spinning droplet tensiometry) was experimentally studied in Ref. [18], where the existence of the dynamic surface tension at a miscible interface was confirmed. The spreading of a miscible interface in a vertical cuvette was experimentally studied in Ref. [19], where it was noted that the rate of interface spreading does not obey the Fick's law. For the mixture of 1-butanol/water, the spreading rate was proportional to  $t^{0.09}$ , and the spreading occurred into the component not saturated with other component. For the isobutyric acid/water mixture in the conditions above the critical point (when both liquids are miscible in all proportions), the spreading occurred with the rate  $t^{0.06}$  into the direction of the isobutyric-acid-rich phase. In another work by the same group [20], it was found that the spreading of the monomer/polymer boundary obeys the Fick's law but only after some transitional period that lasted for up to 30–60 min. The latter experiments were fulfilled with the low molecular weight polymers.

The theoretical modelling of the diffusive dissolution of a small droplet enclosed in a capillary was conducted by Ugrosov et al. [21]. In their work, the process of dissolution was split into two separate steps. During the first step, that was assumed to be infinitely short, the concentration within the droplet adjusted the saturation level. The concentration tails were formed in the medium surrounding the droplet. It was assumed that the dissolution of the droplet (i.e. its shrinkage) occurred due to Fickian diffusion happening at the concentration tails. This Fickian diffusion was the long second step of the dissolution process. No experimental verification of this theory was reported.

To conclude this introductory section, we wish to mention that a proper understanding of how the diffusion at the solute/solvent boundary occurs is of great practical importance. This is needed for accurate modelling of the mixing of chemicals in various chemical engineering processes, where such a mixing is required prior to chemical reactions occur. The dynamics of the solute/solvent mixtures enclosed into capillaries is important for modelling of such processes as vegetable solvent extraction (when the solvent is used to wash out the solute from the vegetable-based porous media), aquifer remediation (e.g. pumping of solute through contaminated soils), and enhanced oil recovery based on the miscible displacement and CO<sub>2</sub> sequestration [22–25].

## 2. Fick's law results

We aim to reproduce the evolution of a binary mixture that saturates a horizontal capillary with open ends. The idea to investigate the diffusion within the capillary was discussed in [8],

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