Modelling of the rise and absorption of a fluid inclusion

Anatoliy Vorobev [a],[*], Elena Khlebnikova [b]

[a] Faculty of Engineering and the Environment, University of Southampton, Southampton SO17 1BJ, UK
[b] Department of Fuel Engineering and Chemical Cybernetics, Institute of Natural Resources, National Research Tomsk Polytechnic University, Tomsk 632050, Russia

ARTICLE INFO

ABSTRACT

The buoyancy-driven rise of a small single fluid inclusion in a viscous liquid that is enclosed in a container of the cylindrical shape is numerically modelled. It is additionally assumed that the inclusion is slowly absorbed by the surrounding liquid. The phase-field approach is used as a physics-based model for the description of the thermo- and hydrodynamic evolution of a miscible heterogeneous binary mixture. The interplay of the effects of absorption and inclusion's motion are investigated. We found that the dissolution of a nearly spherical inclusion does not occur evenly over its surface. The interfacial diffusion is stronger at the inclusion's top cap. The matter absorbed by the liquid does not quickly penetrate into the bulk of the ambient phase, it accumulates behind the inclusion forming a concentration wake. We found that during the rise the inclusion's speed grows. The speed and the acceleration of the inclusion strongly depend on the absorption rate, so the inclusion rises faster at the higher absorption rates. This effect is explained by the action of the Marangoni stress that is developed due to non-uniform mixture composition along the inclusion's surface. We also found that the rise of the inclusion in a closed container is accompanied by the recirculation flow that is developed near the inclusion and that rises upwards with the inclusion. In the limit of negligible absorption (higher Peclet numbers) the convergence to a constant terminal speed of an immiscible inclusion is observed.

© 2018 Elsevier Ltd. All rights reserved.

1. Introduction

On the basis of the phase-field approach we model the evolution of a gaseous or liquid inclusion that rises in another liquid. It is additionally assumed that the inclusion is slowly absorbed by the ambient liquid, and the effects of the absorption on the inclusion's speed, the inclusion's shape, and the effects of the inclusion's motion on the rates of absorption are investigated.

The evolution of a single inclusion is studied to comprehend the mixing dynamics of liquid/liquid and gaseous/liquid substances. The complete and fast mixing is a frequent pre-requirement for chemical interactions, and thus is highly desired in the majority of chemical engineering processes. In particular, it is known that slow and limited miscibility of gaseous species in liquids limits the reaction rates and the amounts of the reactants that partake in the process, forcing an extensive supply of the reactants, and thus leading to the problems of separation of products from non-reacted feedstock substances. To increase the area of contact of the phases, the reactants can be fed into a liquid-filled reactor in the form of small inclusions (the so called bubble column reactor).

A particular example would be the process of benzene alkylation that is used for production of ethylbenzene (a key intermediate for styrene production) with the yearly global demand exceeding 25 million tonnes [1,2]. Almost all ethylbenzene is synthesized from benzene and ethylene. In one of the variations of the process the alkylation is performed in the presence of mineral (Lewis) acids that are used as catalysts [1,3,4]. These acids are highly toxic and corrosive and are frequently neutralised at the end of the reaction producing salts that need to be disposed. For the alkylation, benzene and catalyst are supplied in the liquid form, while ethylene is fed in the gaseous form as bubbles that rise in the reactor. Slow absorption of ethylene bubbles by the liquid phase limits the reaction rates, and intensification of the absorption can significantly reduce the usage of the reactants, including the catalyst, thus reducing the cost of the products and the environmental impact of the technology.

Another chemical engineering problem of the considerable interest and importance is the CO_2 absorption by aqueous amine solutions that is considered as one of the most promising techniques for the CO_2 capture [5,6]. Optimisation and scale-up of this process is again significantly hampered by the low and slow miscibility of CO_2.

* Corresponding author.
E-mail address: A.Vorobev@soton.ac.uk (A. Vorobev).

Modelling of the dynamics of a single inclusion is the focus of the current study. The characteristics of a rising inclusion (its speed and shape) are affected by the different parameters that define the properties of both phases, such as density, viscosity and surface tension. The hydrodynamic aspects of such motion have been thoroughly studied in numerous theoretical and experimental works, see e.g. [7–19] and reviews [20,21]. One of the current focuses of the similar studies is the development of new numerical models capable of accurate tracking of the liquid/bubble interfaces, as owing to a wide range of the available experimental data the rise of a single inclusion is considered as an excellent test for verification of the new numerical tools (see e.g. [22–26]). The phase-field approach was also proved to be an efficient method for the accurate modelling of complex shape transformations of a rising inclusion in a viscous liquid with large density and viscosity contrasts, see e.g. works [27,28].

The rise of an inclusion that is absorbed by the ambient liquid was also examined in a number of experimental and numerical works. For instance, in [29,18] the equation for the species balance is solved to determine the concentration fields in the ambient phase and thus to calculate the diffusion fluxes from a quasi-steady bubble (i.e. when all fields around the bubble can be regarded as steady) under assumption that the change of the bubble's shape (and size) due to interfacial diffusion is negligible. The change of the bubble's size is taken into account in papers [30,31], although under the assumption that the dissolved material is homogeneously spread in the surrounding liquid. This approach was further extended in paper [32] by taking into account the changes in the size of the bubble upon dissolution, although the bubble was assumed to remain spherical. In a recent work [33], the VOF method was modified by the addition of the source term, that takes into account the dissolution of the bubble, into the equation for the volume fraction function.

In the papers referred above the dissolution rate is defined as the difference between the concentration of the dissolved substances in the bubble's phase and the saturation level in the surrounding liquid. It should be also emphasised that the primary focus of these works is on the dissolution rates from a rising bubble, assuming that the dissolution is rather weak so its influence on the rising dynamics is neglected. Although we should mention that an addition of soluble surfactants changes the fluid velocity fields near rising bubbles, thus altering the speeds of bubbles' rise, see e.g. [34,35,20,36].

In the current work we develop a new model that accurately describes the motion and the dissolution of the inclusion in a viscous liquid, fully resolving the flow fields within the inclusion and in the ambient phase, and tracing the transformations of the inclusion's shape due to mechanical action and due to dissolution/absorption [37]. We also take into account the smearing of the interfacial boundary upon the dissolution, and the dynamic changes in the surface tension. The rate of interfacial diffusion is determined though the extended Fick's law, i.e. through the difference in the chemical potential, taking into account the effect of barodiffusion.

2. Governing equations. Phase-field approach

In the current work the phase-field approach is employed as a physics-based model capable of accurate description of the thermo- and hydrodynamic evolution of the binary mixture. The interface separating two liquids is represented as a transitional boundary of a finite thickness. The concentration field C, that is defined as the mass fraction of one component in the mixture, is used to trace the evolution of the interfacial boundary. The specific free energy function is defined as a function of concentration and concentration gradient [38],

$$f(C, \nabla C) = f_0(C) + \frac{\epsilon}{2}(\nabla C)^2. \tag{1}$$

Here the second term takes into account the surface tension effects. The role of this term is defined by the capillary constant ϵ, which is assumed to be sufficiently small so to make these effects negligible everywhere save for the places of large concentration gradients, i.e. where interfaces are located.

The classical part of the free energy function, f_0, should define the possible states of the mixture. For instance, this part can be determined by the Landau formula,

$$f_0(C) = a(C - C_{cr})^2 + b(C - C_{cr})^4. \tag{2}$$

This expression would be particularly suitable to represent the equilibrium states of binary mixtures with the so-called upper critical temperature (when the mixture is homogeneous in equilibrium above the critical temperature and may be heterogeneous below the critical temperature), especially, the states of the mixture in the vicinity of the consolute point (defined by the concentration C_{cr}). The phase diagram of such a mixture is defined by the equation, $\mu_0 = df_0/dC = 0$, or, $(C - C_{cr})^2 = -a/(2b)$. When $a/(2b)$ is negative, the latter equation has two solutions,

$$C = C_{cr} \pm \left(\frac{-a}{2b}\right)^{1/2}, \tag{3}$$

that are associated with two components of the mixture. If $a/(2b)$ is positive then the equation has only one homogeneous solution. Hence, the parameter $a/(2b)$ can be interpreted as the difference of the temperature from the critical point ($T - T_{cr}$).

We further assume that the behaviour of a mixture with the consolute point is examined. We however want to extend our consideration assuming that the binary mixture may occupy any physically possible thermodynamic state, that are not obligatory located near the critical point. The parameters a and b in our work are treated as the two phenomenological coefficients with the values to be taken so to provide better matching with the experimental data. We however assume that b remains positive while a is either positive or negative depending on whether the binary system is single- or two-phase in equilibrium. In other words we extend the usual expectations allowed for the values of a and b near the consolute point to all possible thermodynamic states of the binary mixture.

For convenience, we shift the reference point for the concentration field as follows, $C \rightarrow (C - C_{cr})$. For simplicity we also assume that the phase diagram is symmetrical with the critical concentration $C_{cr} = 1/2$. The values of the new concentration then vary within the range $[-1/2; 1/2]$.

In the presence of strong gravity-induced gradients in the field of concentration, or in the presence of strong flows, expression (2) becomes less convenient, as in these cases the numerically calculated values of the concentration can be outside of the range of concentrations that correspond to the pure components ($\pm 1/2$).[1] In [39,40] the other free energy function is used,

$$f_0 = \left(a - \frac{3}{2}b\right)C^2 + \frac{3}{4}b\left[\left(\frac{1}{2} + C\right)\ln\left(\frac{1}{2} + C\right) + \left(\frac{1}{2} - C\right)\ln\left(\frac{1}{2} - C\right)\right]. \tag{4}$$

The logarithmic terms of this function, that are written similarly to the regular solution model frequently used in the theory of polymers [41], limit the values of concentration to the range $[-1/2; 1/2]$. In the case the symmetrical phase diagram, with the consolute point at $C = 0$ (or for the old reference point, at

---

[1] The similar over-shootings are allowed by the shape of the free energy function (2), and such over-shootings are actually regularly observed in the numerical results obtained on the basis of the phase-field approach.