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Modeling and Simulation of Diffusion-Convection-Reaction in Heterogeneous Nanochannels Using OpenFOAM

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Abstract. We present a finite volume implementation of a phase field method in OpenFOAM as a tool to simulate reactive multiphase flows on heterogeneous surfaces. Using this tool, we simulate the formation and growth of a droplet due to a chemical reaction on a hydrophilic catalytic patch surrounded by a hydrophobic wall. We compare the growth dynamics with a quasi-static growth model from literature and show that they qualitatively agree.

INTRODUCTION

Multiphase reactive flows in micro/nanochannels are important in many applications such as catalysis [1] or enhanced oil recovery [2]. The distribution of different phases in these small channels depends on the interfacial energies between the different phases and between the phases and the channel walls. Often, the properties of the wall are not uniform, such as in the pores of a catalyst pellet, where the reactive catalytic areas have different wetting properties from the surrounding walls. The morphology of the flow can influence the mass transfer to the wall and hence it is important to understand the correlation between the surface heterogeneities and the phase distribution. Many computational fluid dynamic methods, such as the volume of fluid method or the level set method, have been used to simulate multiphase flows on heterogeneous surfaces [3]. The Lattice-Boltzmann method has been used to simulate multiphase reactive flows [4]. However, no method for multiphase flows has so far been used to model surface heterogeneities due to wetting and chemical reactions simultaneously.

In this paper, we propose a phase field model to simulate multiphase flows on heterogeneous surfaces. We consider a toy-problem in which a one-component fluid reacts at a hydrophilic catalytically-active patch in a nanochannel to form another one-component fluid that is partially miscible with the first fluid. This leads to the formation of a droplet on top of the patch. After reaching a critical size, the droplet spreads over the surrounding hydrophobic walls. We show that our simulations qualitatively agree with a previously reported equilibrium model.
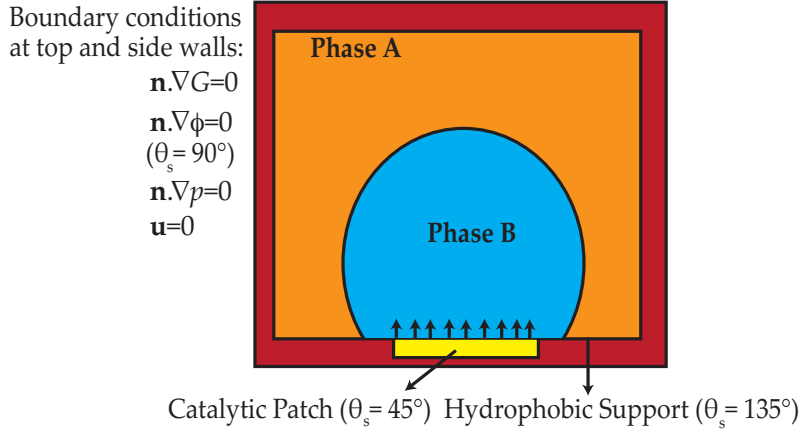
PROBLEM DESCRIPTION

The 2-D domain is shown in figure 1. The size is 100 nm$\times$100 nm, and the width of the catalytic patch is L =40 nm. This is a closed system with a hydrophilic catalytic patch (static contact angle $\theta_s = 45°$) surrounded by a hydrophobic wall ($\theta_s = 135°$) at the bottom and homogeneous surfaces ($\theta_s = 90°$) at the top and side walls. Initially, only phase A is present. This phase reacts at the catalytic patch according to a simple first order equi-molar irreversible reaction $A \rightarrow B$, where the reactant phase A and the product phase B have the same molar mass, density ($\rho = 1000\,\text{kg/m}^3$) and viscosity ($\mu = 0.0316\,\text{kg/m·s}$). The rate constant of the surface reaction is $k = 0.0316\,\text{m/s}$. The surface tension is $\sigma = 0.02\,\text{N/m}$ and the diffusivity of the two phases as represented by the mobility is $M = 1 \times 10^{-8}\,\text{m}^2/\text{s}$.

PHASE FIELD METHOD

We use a standard phase field method for two immiscible fluids with equal density (model H in [5]):

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

Boundary conditions
at top and side walls:
$\mathbf{n}.\nabla G = 0$
$\mathbf{n}.\nabla\phi = 0$
$(\theta_s = 90°)$
$\mathbf{n}.\nabla p = 0$
$\mathbf{u} = 0$

Phase A

Phase B

Catalytic Patch ($\theta_s = 45°$) Hydrophobic Support ($\theta_s = 135°$)

FIGURE 1. Simulation domain with different boundary conditions

$$\frac{\partial \rho \mathbf{u}}{\partial t} + \nabla \cdot (\rho \mathbf{u}\mathbf{u}) = -\nabla p + \mu \nabla^2 \mathbf{u} + F_s \tag{2}$$

$$\frac{\partial \phi}{\partial t} + \nabla \cdot (j + \mathbf{u}\phi) = 0 \tag{3}$$

Here, $\mathbf{u}$ is the volume-averaged velocity, $\phi (\in [0, 1])$ is the volume fraction of phase A, F_s is the surface tension force modeled as $F_s = -6\sqrt{2}\sigma\varepsilon\nabla \cdot \left(\frac{\nabla\phi}{|\nabla\phi|}\right) \mid \nabla\phi \mid \nabla\phi$ with ε a parameter that scales with the thickness of the interface, see *e.g.* [6]; $j = -M\nabla G$ is the diffusive flux with G the chemical potential. This potential is obtained from a double-well free energy functional F commonly modeled as $F = (\phi - a)^2 (\phi - b)^2/4$ [5, 6] with a and b the roots of F that determine the miscibility between the phases. To allow a one-way 1% miscibility of A in B, we use $a = 0$ and $b = 0.99$. The chemical potential can then be calculated as [5] $G = \delta F/\delta\phi - \varepsilon^2\nabla^2\phi$.

The boundary conditions for the chemical potential, the pressure, the velocity, and the phase fraction at the side and top wall are shown in figure 1. The boundary conditions at the bottom wall take care of the surface heterogeneities due to different wetting properties and surface reactivities. To simulate the different wetting properties, we apply the commonly used natural boundary condition (NBC) [7]

$$\varepsilon \frac{\partial \phi}{\partial n} + \frac{1}{\sqrt{2}}\phi (\phi - 1) cos\theta_s = 0 \tag{4}$$

where we neglect the 1% miscibility in its derivation. Note that this indeed yields $\mathbf{n} \cdot \nabla\phi = 0$ at the top and side walls for which we use $\theta_s = 90°$. The surface reaction at the catalytic patch is modeled through the boundary condition for the chemical potential as [8]

$$-\mathbf{n} \cdot M\nabla G = k(1 - \phi) \tag{5}$$

which balances the diffusive flux at the catalytic patch with the surface reaction. We complement these boundary conditions with a boundary condition for velocity $\mathbf{u} = 0$ and for pressure, where the latter ensures a pressure gradient consistent with the velocity boundary condition known as the "*fixedFluxPressure*" boundary condition in OpenFOAM.

The implementation of the phase field method is done by modifying the standard Volume of Fluid solver (*interFoam*) of OpenFOAM. We use the PISO algorithm for pressure-velocity coupling. A first order Euler implicit discretization is used for the temporal derivatives. For the spatial derivatives, an explicit second order Gauss linear and a hybrid van Leer scheme are used. Adaptive time stepping based on the Courant number is implemented, where we use a Courant number limit of 0.001. This severe restriction is necessary due to the explicit discretization of the fourth order diffusion equation [$\Delta t \sim O(\Delta x^4)$] and we observe unstable solutions at higher values. All boundary conditions are implemented using the groovyBC functionality.

SIMULATION DETAILS

The simulations are performed with a non-dimensional implementation of the solver. Considering the reaction velocity k as the characteristic velocity, the length of the catalytic patch L as the characteristic length, and using $\varepsilon = 1$nm for the interface thickness parameter yields the following dimensionless groups:

$$Pe = \frac{kL}{M} = 0.13, Ca = \frac{\mu k}{\sigma} = 50 \times 10^{-3}, Re = \frac{\rho kL}{\mu} = 4.0 \times 10^{-5}, We = \frac{\rho k^2 \varepsilon}{6\sqrt{2}\sigma} = 5.9 \times 10^{-9}, Cn = \frac{\varepsilon}{L} = 25 \times 10^{-3} \quad (6)$$

All simulations are done in 2-D (dimensionless domain size is 2.5×2.5) and on a uniform hex-mesh with the mesh size $\Delta x = \Delta y = Cn$.

RESULTS AND DISCUSSION

The evolution of the droplet interface is shown in figure 2(a) and reveals three regimes: In regime 1, the droplet grows only on the catalytic patch until its base width equals the width of the patch. In regime 2, the droplet pins at the edge of the patch, assumes an ellipsoidal shape and grows in size. This regime transitions to regime 3 when the contact angle of the droplet reaches the static contact angle of the hydrophobic wall such that the droplet de-pins from the edge of the patch. In regime 3, the droplet grows on the hydrophobic patch with a contact angle close to the static contact angle. These three regimes are in good agreement with those reported by Lenz and Lipowsky [9], who developed an equilibrium model for droplet growth on a heterogeneous surface.

To quantitatively analyze our simulations, we show the evolution of the contact angle and the base width (made dimensionless with L) as a function of the droplet area (made dimensionless with L^2) in figure 2(b). In regime 1, the base width grows rapidly until the droplet covers the entire catalytic patch. In regime 2, we observe that the growth of the droplet is not completely constrained by the patch, as part of the diffuse interface spreads over the hydrophobic support leading to a base width slowly growing larger than unity. In this regime, the contact angle increases rapidly and approaches the equilibrium hydrophobic patch contact angle. After reaching a certain critical droplet area and contact angle, the droplet transitions to regime 3 and the diffuse interface no longer touches the edge of the patch. This transition is characterized by a simultaneous change in growth rate of both the base width and the contact angle as highlighted in the inset of figure 2(b) and defines the transition base width. In regime 3, the contact angle remains roughly constant and the base width increases roughly with the square root of time.

Comparing these results to the equilibrium model by Lenz and Lipowsky [9], the first difference we observe is a slight deviation in the second growth phase, where the model predicts no growth in base width. We postulate that this deviation is due to the finite interface thickness. To understand the effect of numerical interface thickness on the dynamics, we performed additional simulations with a different interface thickness. The transition base width linearly depends on the numerical thickness as shown in figure 2(c). This confirms that the droplet width growth in regime 2 is due to the finite numerical interface thickness and the model approaches the equilibrium model, i.e. transition base width equals 1, in the limit of $\Delta x \to 0$. A second difference between our simulations and the equilibrium model is the evolution of the contact angle in regimes 1 and 3, where the model predicts a fixed contact angle equal to the equilibrium contact angle of the catalytic patch and hydrophobic wall respectively. We explain this difference by the fact that, unlike the model, our simulations are out of equilibrium such that the shape of the droplet is influenced by re-circulations in and around the droplet, which are most prominent close to the contact line as shown in figure 2(d).

CONCLUSION

In this paper, we presented a phase field approach to model multiphase reactive flows in nanochannels and its implementation in OpenFOAM. To validate our model, we considered a system with a simple reaction on a heterogeneous surface. Our results are in qualitative agreement with the equilibrium model and validate the implementation of the phase field method with chemical reactions on a heterogeneous surface. An extension of the method to different density and viscosity cases is under development such that the method can be extended to complex reactions and potentially used for many other applications.
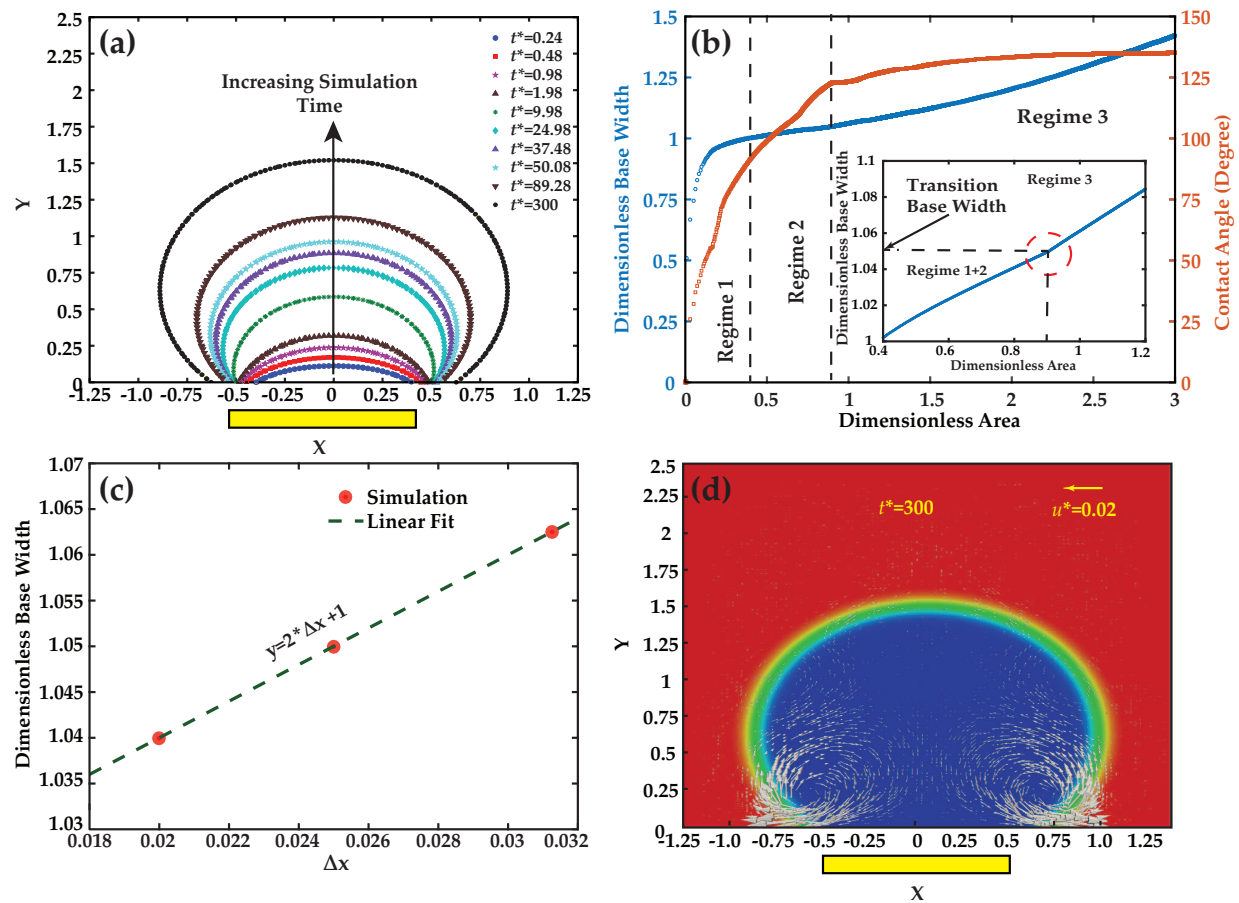
FIGURE 2. (a) Evolution of droplet interface (contour of $\phi = 0.5$). The catalytic patch position is shown as a yellow box. For $t^* < 10$, the droplet grows only on the catalytic patch (regime 1). Between $10 < t^* < 40$, the droplet is pinned at the catalytic patch edge and its contact angle increases with time (regime 2). For $t* > 40$, the droplet is de-pinned from the catalytic patch edge and grows on the hydrophobic surface (regime 3) with a contact angle roughly equal to the static contact angle. (b) Base width and contact angle of the droplet as a function of its area. Growth regimes 1, 2 and 3 are highlighted. The change in slope for the base width (encircled in the inset) defines the transition from regime 2 to 3 as well as the transition base width. (c) Transition base width for different numerical grid sizes. (d) Velocity field at $t^* = 300$ showing re-circulation patterns near the contact line.

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