# Discrete Duality Finite Volume method for Cahn-Hilliard equations with surfactants

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This work focuses on the numerical analysis of a phase field model with surfactants, originally introduced by Laradji et al. [2]. The model describes the phase separation dynamics between water and air in the presence of surfactants, and has numerous applications in pharmacology, biology, and physics, among others. We represent this dynamics using two coupled Cahn-Hilliard equations. Cahn-Hilliard equations model the phase separation process of two non-miscible fluids, for which the fluids spontaneously separate forming sub-domains of pure phases [1]. We therefore use a first Cahn-Hilliard equation to describe the phase separation dynamics between water and air. We restraint ourselves to the study of the evolution of a single fluid concentration $\phi = \phi_1$ (called order parameter), the behavior of the other one being given by $1-\phi$. Surfactants (diminutive form of *Surface Active Agents*) are molecules soluble in water, highly present in nature. We model their dynamic through a second Cahn-Hilliard equation, representing surfactants as a fluid separating from water. We let $c$ denote the surfactant concentration, and consider the following probrem : Find $\phi : (0,T)\times\Omega \to \mathbb{R}$ and $c : (0,T)\times\Omega \to \mathbb{R}$, such that

$$\begin{cases} \partial_t \phi = M_\phi \Delta \mu, & \forall (t,x) \in (0,T)\times\Omega, \\ \mu = -\epsilon_\phi \Delta \phi + \dfrac{1}{\epsilon_\phi} f'_\phi(\phi) + \partial_\phi W(\phi, c), & \forall (t,x) \in (0,T)\times\Omega, \\ \partial_t c = M_c \Delta \eta, & \forall (t,x) \in (0,T)\times\Omega, \\ \eta = -\epsilon_c \Delta c + \dfrac{1}{\epsilon_c} f'_c(c) + \partial_c W(\phi, c), & \forall (t,x) \in (0,T)\times\Omega, \\ \nabla\phi\cdot\vec{\boldsymbol{n}} = \nabla c\cdot\vec{\boldsymbol{n}} = \nabla\mu\cdot\vec{\boldsymbol{n}} = \nabla\eta\cdot\vec{\boldsymbol{n}} = 0, & \forall (t,x) \in (0,T)\times\partial\Omega, \end{cases}$$

where $\Omega$ is a bounded open set of $\mathbb{R}^d$ ($d = 2$ or 3), $\epsilon_\phi$ and $\epsilon_c$ represent interface thicknesses associated with $\phi$ and $c$, respectively, and the diffusion coefficients $M_\phi$ and $M_c$ are physical parameters called mobilities. The potentials $f_\phi(\phi) = \frac{1}{4}(\phi^2-1)^2$ and $f_c(c) = c^2(1-c)^2$ are classical polynomial double-well potentials that ensure phase separation. We carefully constructed the coupling potential to ensure the well-posedness of the problem and the stability of the numerical scheme, all while maintaining physical validity [3]. Specifically, we define it as $W(\phi,c) = -\alpha|\nabla\phi|^2 c + \beta\phi^2 c - \gamma\phi^3 c + \delta|\nabla\phi|^4$, where the first three terms model the interaction between air, water, and surfactants, and the last guarantees stability. Our main goal is to prove the convergence of the approximate solution to the continuous one. From a mathematical perspective, this is particularly challenging due to the strong nonlinearities in the coupling potential, which require a strong convergence of the discrete gradient. We therefore adopt the Discrete Duality Finite Volume (DDFV) method to discretize the problem, which offers greater robustness compared to the Two-Point Flux Approximation scheme. We begin by proving the existence and uniqueness of a solution to the continuous problem, a result that enables us to handle the most nonlinear terms. The convergence of the remaining terms is established using discrete results, such as energy estimates, *a priori* bounds on the discrete solutions and compactness arguments. Finally, we validate the model through numerical simulations.

[1] J.-W. Cahn, J.-E. Hilliard. *Free energy of a nonuniform system. I. interfacial free energy.* The Journal of Chemical Physics, **28(2)**, 258–267, 1958. doi :10.1063/1.1744102.

[2] M. Laradji, H. Guo, M. Grant, M. J. Zuckermann. *The effect of surfactants on the dynamics of phase separation.* Journal of Physics : Condensed Matter, **4(32)**, 6715, 1992.

[3] J. Zhang, C. Chen, J. Wang, X. Yang. *Efficient, second oder accurate, and unconditionally energy stable numerical scheme for a new hydrodynamics coupled binary phase-field surfactant system.* Computer Physics Communications, **251**, 107122, 2020.

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