A MULTISCALE STUDY OF MICROWAVE ASSISTED HETEROGENEOUS REACTIONS

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Abstract

In this work, we develop a multiscale computational framework to explore the microwave heating in multiphase systems, i.e., solid particles dispersed in a fluid, and their impact on heterogeneous reactions. To handle the large disparity of length scales between the particle size and the complete domain, we employ a number of coarse-graining techniques, such as the homogenization theory, to calculate the dielectric properties of the representative continuum medium. The resulting formalism is applied to a range of particle shapes, particle arrangements, and volume fractions. We also show that the "mixing formulae" commonly utilized in the literature are only applicable to spherical particles and fail in other cases. The study allows to investigate the temperature distribution and the reactions rates in multiphase systems in detail, while keeping the computationally cost tractable.

Keywords

Microwave Heating, Heterogeneous Reactions, Multiscale modeling, Coarse-graining.

Introduction

In many ways traditional chemical industry has saturated in terms of productivity, yield, and energy efficiency. Novel ways to bring breakthrough, such as enhanced energy efficiency or utilizing alternative energy forms, in chemical industries are required. Microwaves provide an alternative to fossil fuels as an energy source and rapid heating of the reaction system. With its first application in 1980s in the field of organics synthesis, today the application of microwaves is being explored in a variety of chemical processes, such as biomass-based renewable chemicals, pharmaceutical drug discovery, and waste valorization. Still, the fundamental knowledge of microwaves assisted chemical processes is limited. Experimental studies alone do not provide a detailed picture of the microwave heating and its coupling with the reacting process. In this regard, modeling and simulation tools can provide detailed insights about the underlying phenomena and a framework to design, optimize, and scale-up of microwave reactors. Many chemical processes involve heterogeneous catalysts and exhibit a large separation of scales, from the active phase to the pellet to the chemical reactor, rendering the computational cost of detailed simulations prohibitive. The focus of this study is to develop an affordable multiscale computational framework for multiphase reaction systems possessing a large separation of scales. To this end, we employ various coarse-graining approaches, such as the Maxwell Garnett formula (Markel, 2016) and the homogenization theory (Pavliotis and Stuart, 2008), to obtain effective dielectric properties of a two-phase system. The resulting properties are used to simulate the two-phase system as a continuum. This strategy allows us to obtain a quantitate description of the temperature distribution and the resulting reaction rates in a computationally affordable manner. Computational results are compared to experimental data from our lab for a slurry microreactor using inert carbon nanoparticles as well metal nanoparticles on various supports.

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Methodology

COMSOL RF Multiphysics commercial software is used to perform the simulations of the microwave heating. It solves the frequency domain form of Maxwell's equations via the finite element method. Outside boundaries of the computational domain are made microwave transparent using the *perfectly matched layer* and the *scattering boundary condition* to truncate the computational domain to a finite-sized domain. Particles are distributed in a uniform fashion in a continuous medium. First, particle-resolved simulations of the microwave heating of the two-phase system are performed. Then the commonly used Maxwell Garnett formula is utilized to predict the *effective dielectric properties* (ε_m) using the dielectric properties of both the dispersed (ε_d) and continuous (ε_c) phase. ε_m is used to represent the two-phase system as a single continuous phase. Coarse-grained simulations of the microwave heating of this representative single continuous phase are performed and compared with spatially resolved simulations of the two-phase system. The framework is extended to use modern coarse-graining methods, such as the homogenization theory.

Results and Discussion

For demonstration purposes, two particles shapes are selected: 1) spherical (diameter=100 μm) and 2) cylindrical (diameter=50 μm, length=200 μm). The simulation configuration for the two-phase system with the cylindrical particles as the dispersed phase is shown in Fig 1(a). A low microwave absorbing continuous phase is chosen with ε_c=2, whereas for the dispersed phase, the dielectric constant, ε'_d is fixed at 10 while varying the tanδ from 0.1 to 1. Sufficiently small mesh size is used to resolve each particle. Figure 1(a) shows the distribution of the electric field norm, E_{norm} for the case of cylindrical particles. It can be seen that near the edges of the top and bottom faces of the cylinder, E_{norm} is much higher than the rest of the particle showcasing the impact of particle shape on the distribution of the electric field. As the microwave heat source, Q is proportional to E^2_{norm}, the shape of the particle also impacts their heating rate.

We simulate the two-phase system as well as the representative continuous phase whose dielectric properties are calculated using the Maxwell Garnett formula. An average heat source, $\langle Q \rangle$, over the entire domain is calculated. The deviation in the predictions of $\langle Q \rangle$ using the representative continuum phase and the fully-resolved two-phase system are calculated for both the spherical and cylindrical particles and shown in Fig. 1(b). Figure 1(b) clearly shows that Maxwell-Garnett formula works very well for the spherical particles, whereas for the cylindrical particles large errors are obtained. To remedy this and accurately account for the effect of particle shape and their arrangement, we employ homogenization theory and obtain the effective medium properties. For this purpose, the repetitive unit in the multiphase system is selected, and the numerical solution of the microwave heating of this repetitive unit is used to calculate the effective medium properties. The model is extended to reacting systems and results are compared to experimental data from our lab. It is also demonstrated how to use the model to deduce particle temperature from those of solution, obtained with an optical fiber probe.

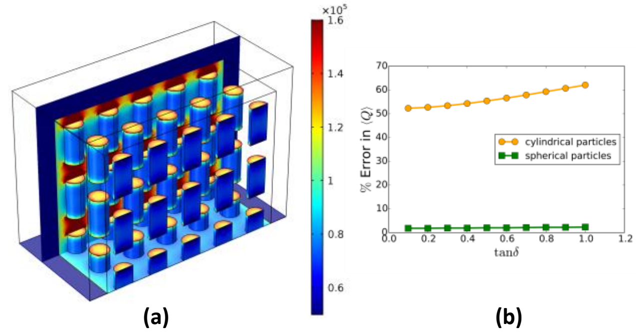

Figure 1. (a) Simulation configuration along with the E_{norm} *for cylindrical particles (*ε'_d *=10 and tan*δ*=0.5) as the dispersed phase; (b) Percentage error in the prediction of* $\langle Q \rangle$ *using the Maxwell Garnett formula.*

Conclusions

In this work, we show that the commonly used Maxwell Garnett formula to get the effective dielectric properties of a multiphase system does not work for non-spherical particles, which are encountered in many practical applications. To accurately capture the reaction rate during the microwave heating of a heterogeneous system, quantitative information about the temperature distribution is necessary. We employ homogenization theory to obtain the effective properties for various particle shapes and arrangements, allowing us to obtain the temperature distribution and thus the reaction rates in heterogenous catalytic systems in a computationally affordable manner. Comparison to experimental data will be demonstrated.

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References

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