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Modeling the coupling of reaction kinetics and hydrodynamics in a collapsing cavity

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ABSTRACT

We introduce a model of cavitation based on the multiphase Lattice Boltzmann method (LBM) that allows for coupling between the hydrodynamics of a collapsing cavity and supported solute chemical species. We demonstrate that this model can also be coupled to deterministic or stochastic chemical reactions. In a two-species model of chemical reactions (with a major and a minor species), the major difference observed between the deterministic and stochastic reactions takes the form of random fluctuations in concentration of the minor species. We demonstrate that advection associated with the hydrodynamics of a collapsing cavity leads to highly inhomogeneous concentration of solutes. In turn these inhomogeneities in concentration may lead to significant increase in concentration-dependent reaction rates and can result in a local enhancement in the production of minor species.

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1. Introduction

There has been revived interest in the chemical effects of high intensity sound waves, namely sonochemistry, since its discovery decades ago [1]. Sonochemistry does not arise from the direct interaction between sound waves and chemical species but via acoustic cavitation [2]. Cavitation is a nonlinear acoustic effect whereby vaporous or gaseous bubbles form as a consequence of pressure variations associated with an acoustic wave. The collapse of unstable cavities leads to extreme conditions of pressure and temperature as well as complex fluid motion such as high velocity fluid jets near solid surfaces. The high energies associated with these extreme conditions can promote chemical reactions and have also been shown to be useful in the synthesis of a large variety of micro and nanoscale structures composed of organic, inorganic materials and biomaterials [3]. The chemical and physical effects of sound can be divided into homogeneous sonochemistry of liquids, heterogeneous sonochemistry of liquid–liquid or solid–liquid systems, with the field of sonocatalysis encompassing all these categories. A complete theoretical understanding of sonochemical processes is not at hand due to the complexity of the coupled physical and chemical processes involved. For instance, a model of the formation of free radicals driven by cavitation requires that the kinetics of free radical formation be linked to the cavity dynamics [4–6]. Recently, Sharma et al. [7] provided a review of important models that couple cavity dynamics, heat transfer, mass transfer and chemical reactions. While the simplest models assume a uniform cavity interior and thus avoid the solution to Navier–Stokes equations [8], it appears important to account for the coupling between the hydrodynamics of the gas in the bubble and associated chemistry [9].

In this paper, we present a model that approaches the coupling between hydrodynamics and chemistry of a collapsing bubble via an extension of the Lattice Boltzmann method (LBM). While at this initial phase we assume the processes to be isothermal, the model considers several aspects of mass transfer including phase change at vapor/liquid interface, diffusion of dissolved species (i.e. solute) as well as changes in concentration of chemical species due to reactions in the liquid and gas core of the bubble. The newly developed LBM offers several advantages compared to other simpler models of cavity dynamics such as the Rayleigh–Plesset equation [10] or the Keller–Miksis equation [11]. LBM can be applied to arbitrary geometry, complex boundaries and offers significant flexibility such as handling of surface interactions, handling multicomponent systems, domain scalability, and algorithmic parallelizability, which are difficult to invoke through commonly available models based on solutions of the governing differential equations. In our study, the basic modeling of bubble formation and collapse is adopted from the work of Sukop and Or [12]. This approach was shown to correctly reproduce key phenomena necessary for the study of cavitation. In addition, the LBM-based model of the hydrodynamics of cavity collapse can be easily linked to chemical transformations of species supported by the cavitating fluid. In this work, we employ two different models of a prototypical chemical reaction. The first one uses deterministic

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rate equations and represents a mean field approximation of the chemical transformations. It is named as coarse model. The second model of chemical reactions is simulated with the kinetic Monte Carlo (kMC) method which accounts for the stochastic nature of the reactions. This latter model, labeled fine, is more realistic than the mean field one but is more computationally demanding.

From a modeling point of view, we show that the kMC used in conjunction with the LBM provides a more detailed and accurate estimation of the kinetic evolution than that given by the mean field model coupled to the LBM. However, this higher degree of realism impacts only the low concentration chemical species (minor species) and does not add significantly to the overall physics and chemistry of reactive-flow near a collapsing cavity. From a sonochemistry point of view, the LBM model coupled with transport of passive chemical species is able to capture the advection of the species at the liquid–vapor interface of the cavity, leading to large enrichment of the region where the cavity collapses and therefore forming highly inhomogeneous distributions of concentration of the chemical species. The coupling of the LBM model with models of chemical reactions leads to enhanced chemical rates in the enriched regions. More specifically the concentration in the minor species can be increase by up to a factor 3 at the core of the collapse cavity.

We present in some details the LBM method for single-component multiphase flow as well as its implementation to simulating advection of dissolved species in Section 2. Section 2 also presents the linear two-species reaction model used for the reactive-flow simulations. In Section 3, we report results of the simulations for cavity collapse in a single-component multiphase fluid. We build on this model to study the effect of advection during cavity collapse on the spatial distribution of passive chemical species supported by the fluid medium. Finally, the coupling between the hydrodynamics of the collapsing cavity, the advection of chemical species and the deterministic or stochastic chemical reactions is characterized via the results of the complete model of the reactive-flow. Conclusions drawn from this study are discussed in Section 4.

2. Methods and model

2.1. Lattice Boltzmann method (LBM) for single-component multiphase flow

We have chosen LBM [13,14] for simulation the cavitation and bubble collapse because of its efficiency and flexibility to incorporate many complex interactions. It can be used for single-component multiphase system such as water and vapor. While details of the method can be found elsewhere [13,15], we adopt the two-dimensional nine velocity component lattice (D2Q9) with velocities e_a. Here $a = 1,3,5,7$ represents velocities along the axial directions, $a = 2,4,6,8$ represents velocities along the diagonal directions and $a = 9$ corresponds to the particle at rest. The magnitudes of the axial components are 1 (lsu ltu^{-1}), the diagonal ones are $\sqrt{2}$ (lsu ltu^{-1}), where lsu stands for a dimensionless lattice space unit and ltu for a lattice time unit. All quantities are expressed in terms of ltu and lsu, linked to the physical system by the following relations:

$$v = (\tau - 0.5)RT\delta t \tag{1}$$

$$c = \delta_x/\delta_y \tag{2}$$

and

$$c_s^2 = RT = c^2/3 \tag{3}$$

where, v is the kinematic viscosity, τ is the relaxation parameter, R is universal gas constant, T is absolute temperature of the system, c is the speed of light in the lattice determined by the spatial (δ_x) and temporal resolution (δ_t), c_s is the speed of sound in the lattice. With the adopted values of τ, c, c_s, we can adjust the geometric physical parameters $\delta x, \delta y, \delta t$ (space/time resolutions) and fluid viscosity (v) to represent a real system. With this configuration, a single particle distribution function f_a will have nine distinct bins. Such a distribution function can visualized as direction-specific fluid densities. The macroscopic density can therefore be summed up from these directional densities.

$$\rho = \sum_{a=1}^{9} f_a \tag{4}$$

The macroscopic velocity u is the average of the microscopic velocities e_a weighted by the directional densities f_a

$$u = \frac{1}{\rho}\sum_{a=1}^{9} f_a e_a \tag{5}$$

This allows passing of the discrete microscopic velocities of the LBM lattice to the macroscopic fluid continuum.

The next operations are streaming/propagation and collision of the fluid particles through distribution functions. The Bhatnagar–Gross–Krook (BGK) approximation is used for collision. Streaming and collision to attain relaxation toward local equilibrium are given by

$$f_a(x + e_a\Delta t, t + \Delta t) = f_a(x,t) - \frac{(f_a(x,t) - f_a^{eq}(x,t))}{\tau} \tag{6}$$

The first part of the above equation represents the streaming from one node to its neighbor and the second term is due to collision. Collision can be thought of as relaxation toward local equilibrium and for the D2Q9 lattice the equilibrium distribution function f_a^{eq} is defined as

$$f_a^{eq}(x) = w_a\rho(x)\left[1 + 3\frac{e_a u}{c^2} + \frac{9}{2}\frac{(e_a u)^2}{c^4} - \frac{3}{2}\frac{u^2}{c^2}\right] \tag{7}$$

where, the weights w_a are $\frac{4}{9}$ for the rest particles $(a = 9)$, $\frac{1}{9}$ for axial directions $a = 1,3,5,7$ and $\frac{1}{36}$ for $a = 2,4,6,8$ for diagonal directions. c is the speed of sound on the lattice, taken as 1/3 (lsu ltu^{-1}).

For multiphase fluid flow, interactions between fluid particles are incorporated. Nearest neighbor attractive interactions is able to simulate the basic phenomena of single-component multiphase fluids. In D2Q9 lattice an attractive force F among nearest neighbor fluid particles is expressed as

$$F(x,t) = -G\psi(x,t)\sum_{a=1}^{9} w_a\psi(x + e_a\Delta t, t)e_a \tag{8}$$

where G denotes the interaction strength and ψ the interaction potential. Whereas alternative forms of potential functions are available, the one used herein is given by

$$\psi(\rho) = \psi_0 \exp(-\frac{\rho_0}{\rho}) \tag{9}$$

where ψ_0 and ρ_0 are constants [16,17]. $G < 0$ gives the attraction between the particles and the force is stronger when the density is higher (leading to surface tension at a vapor–liquid interface).

The force term given by Eq. (8) is incorporated in the LBM simulation by adding a velocity terms to the existing lattice velocity, following the Newton's equation of motion:

$$F(x,t) = \rho(x,t)\frac{d\Delta u_{lr}}{dt} \tag{10}$$

where, $\rho(x,t)$ is the density of fluid at the lattice and Δu_{lr} is the added velocity term due to long range interactions. Recalling the