Macroscale lattice-Boltzmann methods for low Peclet number solute and heat transport in heterogeneous porous media

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This paper introduces new methods for simulating subsurface solute and heat transport in heterogeneous media using large-scale lattice-Boltzmann models capable of representing both macroscopically averaged porous media and open channel flows. Previous examples of macroscopically averaged lattice-Boltzmann models for solute and heat transport are only applicable to homogeneous media. Here, we extend these models to properly account for heterogeneous pore-space distributions. For simplicity, in the majority of this paper we assume low Peclet number flows with an isotropic dispersion tensor. Nevertheless, this approach may also be extended to include anisotropic-dispersion by using multiple relaxation time lattice-Boltzmann methods. We describe two methods for introducing heterogeneity into macroscopically averaged lattice-Boltzmann models. The first model delivers the desired behavior by introducing an additional time-derivative term to the collision rule; the second model by separately weighting symmetric and anti-symmetric components of the fluid packet densities. Chapman-Enskog expansions are conducted on the governing equations of the two models, demonstrating that the correct constitutive behavior is obtained in both cases. In addition, methods for improving model stability at low porosities are also discussed: (1) an implicit formulation of the model; and (2) a local transformation that normalizes the lattice-Boltzmann model by the local porosity. The model performances are evaluated through comparisons of simulated results with analytical solutions for one- and two-dimensional flows, and by comparing model predictions to finite element simulations of advection isotropic-dispersion in heterogeneous porous media. We conclude by presenting an example application, demonstrating the ability of the new models to couple with simulations of reactive flow and changing flow geometry: a simulation of groundwater flow through a carbonate system.


1. Introduction

Numerical simulations of reactive fluid flow through porous media (e.g., karst aquifers, partial melts) should ideally accommodate a multitude of diverse processes: (1) advective-diffusive/dispersive transport of both solutes and/or heat, (2) laminar Darcy flow through low-porosity/permeability fields representing rock matrices and tight fractures, (3) laminar to turbulent open-channel flow through wide fractures and conduits that are specified by detailed flow boundary geometries over time due to dissolution (or melting) and/or mineral precipitation (or crystallization) reactions without the need for remeshing, and (5) implementation of a wide range of chemical and possibly biological reactions and processes. For example, studies demonstrate that the complex interactions between the geometry of karst elements such as conduit tubes, reservoir constrictions and channels [Covington et al., 2009]; chemical reactions [Bahr, 1990], coupled groundwater, solute, and heat transport [Andre and Rajaram, 2005]; as well as consideration of both laminar [Groves and Howard, 1994] and turbulent [Howard and Groves, 1995] flow regimes are important in understanding cave formation and groundwater flow through cave systems. [1] From early in their development, lattice-Boltzmann models have been advanced as a tool for simulating fluid flow through complex pore-space geometries [Succi et al., 1989]. Lattice-Boltzmann methods have been used to simulate fluid flows in a diverse range of porous materials [e.g., Maier et al., 1998; Fredrich et al., 2006; Schaap et al., 2007], including investigations of the behavior of miscible and immiscible multiphase fluids [e.g., Ferréol and Rothman, 1995; Pan et al., 2004] and the role of chemical dissolution [e.g., Kang et al., 2002b; Verhaeghe et al., 2005; Walsh et al., 2008]. Lattice-Boltzmann methods are chosen to

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investigate these processes as these methods are (1) relatively simple to implement, (2) easily adapted to complex fluid flow domains, and (3) readily parallelizable. However, traditional lattice-Boltzmann methods require an exact description of the underlying pore-space geometry, which may be difficult to obtain and, even if known, often demands the use of extensive computational resources [Schaap et al., 2007; Bailey et al., 2009; Walsh et al., 2009b].

To overcome this difficulty, large-scale, or macroscopic, lattice-Boltzmann simulations have been developed that do not require detailed pore space representations, but rather adjust model behavior according to the locally averaged material properties [Freed, 1998; Dardis and McCloskey, 1998a, 1998b; Walsh et al., 2009a]. This is accomplished by introducing macroscale parameters (e.g., pore fraction, permeability), as typically found in standard continuum mechanics models, to the lattice-Boltzmann approach of describing fluid package interactions that integrate to a macroscopic flow behavior. Such macroscale lattice-Boltzmann models retain the ability to simulate Navier-Stokes-type open channel flow where detailed flow domain boundaries, rather than averaged permeabilities, are given and add the option of simulating standard Darcy-type porous medium flow where permeabilities, rather than flow domain boundaries, are provided (Figure 1b). Moreover, these models are able to easily interpolate between regions of Darcy’s Law and full Navier-Stokes fluid flow regimes [Thorne and Sukop, 2004; Walsh et al., 2009a], the simulation of solute and heat transport using these techniques has not been as extensively investigated. A notable exception is the paper by Thorne and Sukop [2004], who employed a partial bounce back model to simulate the transport of heat through a material with heterogeneous permeability. In their model, material permeability is only indirectly coupled to the advective transport through the flow velocity. In a later paper, Walsh et al. [2009a] demonstrated that partial bounce back methods are capable of simulating diffusion in materials with heterogeneous tortuosity. A non-partial bounce back approach was used by Zhang et al. [2002] to model anisotropic dispersion, using a multiple relaxation time lattice-Boltzmann method. However, this, like the other above mentioned methods, failed to account for arguably an equally fundamental material property, namely the effect of heterogeneous porosity on solute and heat transport.

In this paper, we discuss how to introduce pore-space heterogeneity into these macroscopic lattice-Boltzmann models for solute and heat transport. For the sake of simplicity, we concentrate on single relaxation time lattice-Boltzmann models (a discussion of multiple relaxation time lattice-Boltzmann models is presented in Appendix C). This restriction limits the scope of the simulations presented to low Peclet number flows with isotropic hydrodynamic dispersion tensors. We describe several different methods for accounting for heterogeneity and investigate the relative numerical stability of each. We also test the accuracy of these methods through a comparison with analytical solutions and finite element simulations. In Appendix C, we present preliminary research demonstrating how the models in the main text may be extended to simulate flows with anisotropic dispersion tensors by adopting a multiple relaxation time lattice-Boltzmann model. Unless explicitly stated otherwise, any reference to dispersion in the following refers to the isotropic case.

This paper describes two new lattice-Boltzmann methods for simulating macroscale solute and heat transport through heterogeneous porous media containing large-scale fractures or conduits. The first model alters the collision rule in the lattice-Boltzmann simulation to correct the time derivative and diffusive term of the advection isotropic-
dispersion equations. In the second model, the symmetric and antisymmetric components of the lattice-Boltzmann fluid packets are independently weighted to give the desired response. Both new lattice-Boltzmann models deliver the correct constitutive behavior for diffusion-dominated solute and heat transport through a heterogeneous porous medium, as demonstrated by Chapman-Enskog expansions of the governing equations (Appendices A and B) and comparisons with analytical and numerical solutions. An example application, simulating multicomponent (water, CO$_2$, Ca$^{2+}$), reactive flow describing cave formation (speleogenesis) in a limestone (CaCO$_3$) aquifer system, is also provided to demonstrate the ability of the model to deal with evolving pore-space geometries.

The basic lattice-Boltzmann method and the modifications enabling macroscopically averaged lattice-Boltzmann models for porous media flows are presented in section 2. In section 3, we modify the conventional lattice-Boltzmann model for solute transport simulations to yield the correct governing equations for macroscopically averaged lattice-Boltzmann models, simulating solute transport through porous media. Methods for improving the stability of the model in low-porosity media (by employing an implicit formulation of the model and by rescaling the model by the average porosity) are also discussed. Necessary modifications of the models to simulate heat transport are presented in section 4. The new macroscale lattice-Boltzmann model of solute-transport is validated by comparing its results to analytical solutions for one- and two-dimensional solute transport through homogeneous porous media, and to finite element simulations of solute transport through a heterogeneous porous medium (section 5). Finally, an example application, simulation of speleogenesis in carbonate aquifers, is given in section 6, and conclusions are provided in section 7.

### 2. Macroscopic Lattice-Boltzmann Models for Porous Media

A brief overview of lattice-Boltzmann methods, and an introduction to macroscale lattice-Boltzmann methods for modeling porous media are provided in this section. Readers interested in more detailed descriptions of lattice-Boltzmann techniques are referred to Rothman and Zaleski [1997], Wolf-Gladrow [2000], Succi [2001], and Sukop and Thorne [2006]. The latter text also contains an in-depth discussion of macroscopic lattice-Boltzmann models for porous media.

Lattice-Boltzmann models represent fluid flow via a set of fluid packets, $f_i$, that propagate about a regular node lattice. These fluid packets are discrete representations of the single-body particle distribution functions described in the classical Boltzmann equation [Boltzmann, 1872]. The lattice-Boltzmann method may therefore be regarded as approximating the fluid’s microscopic particle dynamics, from which larger-scale classical continuum fluid dynamics emerges as a byproduct. The connection between the microscopic fluid flow description and the macroscopic equations is made in much the same way as the connection between the statistical-mechanics description of a fluid and the macroscopic fluid mechanics by employing a Chapman-Enskog expansion of the underlying microscopic level equations [Chapman, 1916, 1918; Dawson et al., 1993].

Lattice-Boltzmann simulations have been formulated for a range of different lattice types (varying by node connectivity and dimension), and there exists a growing number of techniques for conducting lattice-Boltzmann simulations on irregular meshes [e.g., Guo and Zhao, 2003; Li et al., 2005]. The discussion in this paper focuses on the widely used D1Q3/D2Q9/D3Q19 family of lattice-Boltzmann lattices (where the numerals following D and Q indicate number of lattice dimensions and fluid packet velocities, respectively) described by Qian et al. [1992]. Nevertheless, we anticipate that the methods introduced in the following sections are readily extended to other lattice-Boltzmann meshes and related approaches.

During each time step of a lattice-Boltzmann simulation, fluid packets converging on a given lattice node are redirected according to a collision rule assigned to the node. For example, in the standard single-relaxation lattice-Boltzmann simulation, the collision rule for open, unobstructed regions is

$$f_i(x + \mathbf{c}_i \Delta t, t + \Delta t) = (1 - \Lambda)f_i(x, t) + \Lambda f^{eq}_i,$$

where $f^{eq}_i$ is the local equilibrium population for the fluid packets, $\mathbf{c}_i$ is the lattice velocity associated with the $i$th lattice direction (summarized in Table 1), and $\Lambda$ is a collision frequency related to the kinematic viscosity, $\nu$, by

$$\Lambda = \left[ \frac{3\nu}{c^2 \Delta t} + \frac{1}{2} \right]^{-1},$$

where $c$ is the lattice velocity (i.e., lattice spacing divided by time step duration, $\Delta x/\Delta t$). For the D1Q3/D2Q9/D3Q19 models, the equilibrium populations, $f^{eq}_i$, are

$$f^{eq}_i = \rho w_i [1 + 3 \mathbf{u} \cdot \mathbf{c}_i (1 + 3 \mathbf{u} \cdot \mathbf{c}_i / 2) - 3 \mathbf{u} \cdot \mathbf{u} / 2],$$

where $w_i$ are weighting constants specific to the lattice velocities (Table 1), $\rho = \sum_i f_i$ is the fluid density, and $\mathbf{u} = \frac{1}{\rho} \sum_i f_i \mathbf{c}_i$ is the net velocity of all incoming fluid packets.

At lattice nodes that form part of a no-slip solid-fluid boundary, the fluid packets obey a “bounce back” boundary condition, so-called because it redirects the incoming fluid packets in the opposite direction:

$$f_i(x + \mathbf{c}_i \Delta t, t + \Delta t) = f_i(x, t),$$

where the subscripted $i$ denotes the lattice direction opposite $i$, thus $\mathbf{c}_i = -\mathbf{c}_i$.

Most lattice-Boltzmann simulations model the fluid domain explicitly at the pore scale, as standard collision rules are only capable of representing a binary domain geometry.
composed of open and impermeable regions. While this approach allows small-scale open-channel flow patterns to be resolved, it is impractical for representing large-scale flows in porous media with small pores and large-scale heterogeneities. An alternative approach is to develop a macroscopic lattice-Boltzmann model incorporating the permeability of the medium as a model parameter [e.g., Freed, 1998; Dardis and McCloskey, 1998b]. Rather than a lattice comprising either solid or fluid nodes, in this approach node properties are varied to reflect local permeability. Such models are particularly suited to simulating problems governed by both full Navier-Stokes and Darcy’s Law behaviors, as the one model is able to interpolate seamlessly between regions of flow governed by the two separate regimes. Thus, within the same simulation, detailed flow velocity fields can be resolved in open-channel flow regions or wide fractures, while regions containing smaller-scale pores can be treated as a continuum (Figure 1b).

[15] There are several methods for formulating macroscopically averaged lattice-Boltzmann models; here two are briefly discussed: (1) partial bounce back methods and (2) force-adjusted models. In partial bounce back models an additional pre- or post-collision step is applied to the fluid packets leaving each node [Dardis and McCloskey, 1998a; Thorne and Sukop, 2004; Sukop and Thorne, 2006]. This step redirects a proportion of the fluid packet back toward the original node, simulating a given density of random scatterers in a lattice-gas model [Dardis and McCloskey, 1998a, 1998b]. In force-adjusted models, the macroscopic permeability is simulated by introducing a body force that retards the fluid flow in accordance with the local material properties [Freed, 1998; Kang et al., 2002a]. This body force is introduced into the model by altering the equilibrium fluid packet density equation (equation (3)).

[16] The application given in section 6 uses the partial bounce back model described by Walsh et al. [2009a] to simulate the advecting fluid. The collision rule in this model combines the fluid collision step rule given in equation (1) and the bounce back rule given in equation (4):

\[ f_i(x + c_i \Delta t, t + \Delta t) = (1 - \alpha)[1 - \lambda f_i(x, t) + \lambda f_i^{eq}] + \alpha f_i(x, t), \]

where \( 0 \leq \alpha \leq 1 \) is a model parameter, somewhat analogous to the solid fraction, controlling the permeability of each node. An analytical expression relating \( \alpha \) to the actual physical permeability is provided by Walsh et al. [2009a].

[17] We stress, however, that the method used to simulate solute transport outlined in the following section is independent of the model used to simulate the fluid flow. The partial bounce back method employed here could be replaced with an alternative macroscopic method, or determined independently through another approach. Indeed, the examples discussed in other sections of this paper are based on fluid flows where the velocity of the fluid is held constant for the purpose of comparison with analytical solutions and the COMSOL finite element simulation (section 5).

3. Lattice-Boltzmann Models for Solute Transport in Porous Media

[18] In addition to simulating Navier-Stokes flow, lattice-Boltzmann models are also capable of simulating advection, molecular diffusion, and mechanical dispersion of a dissolved solute. The latter two terms are typically added and jointly termed hydrodynamic dispersion or just dispersion. Mechanical dispersion is often represented as a second order tensor, given by

\[ D_M = \alpha_T \sqrt{\mathbf{u} \cdot \mathbf{u}} \mathbf{I} + (\alpha_L - \alpha_T) \frac{\mathbf{u} \otimes \mathbf{u}}{\mathbf{u} \cdot \mathbf{u}}, \]

where \( \alpha_L \) is the longitudinal dispersion coefficient, \( \alpha_T \) is the transverse dispersion coefficient, and \( \mathbf{I} \) is the identity matrix [Bear, 1979]. As \( 5 \leq \alpha_L/\alpha_T \leq 100 \) [e.g., Perkins and Johnston, 1963; de Marsily, 1986; Ingebritsen et al., 2006], mechanical dispersion, \( D_M \), is highly anisotropic, even if the porous medium is homogeneous, so that dispersion typically requires treatment as a tensor quantity. In contrast, diffusion depends only on concentration gradients and its isotropic nature allows treatment as a scalar diffusion coefficient, \( D \). Thus the total hydrodynamic dispersion is given by \( D_H = D_M + DI \).

[19] The lattice-Boltzmann models introduced here simulate advection and diffusion of a passive solute using an approach first introduced by Dawson et al. [1993]. This method employs a second set of packets, \( g_i \), representing the solute, in conjunction with the fluid packets, \( f_i \). These new solute packets propagate about the lattice in the same fashion as the fluid packets, and are subjected to collision rules similar to those of the fluid phase:

\[ g_i(x + c_i \Delta t, t + \Delta t) = (1 - \lambda)g_i(x, t) + \lambda g_i^{eq}(x, t), \]

where

\[ g_i^{eq} = C g_i[1 + 3 \mathbf{u} \cdot c_i(1 + 3 \mathbf{u} \cdot c_i/2) - 3 \mathbf{u} \cdot \mathbf{u}]/2, \]

and the solute concentration is \( C = \sum_i g_i \). The key difference between these expressions and the collision rule given in equation (1) is that in equation (7) the velocity, \( \mathbf{u} \), is determined by the fluid packets of the advecting fluid, \( f_i \), not those of the solute phase, \( g_i \). As before, the collision frequency, \( \lambda \), governs the rate at which the fluid packets relax toward equilibrium. Here however, for the solute phase, \( \lambda \) is a function of the (isotropic) diffusivity, \( D \), rather than the kinematic viscosity:

\[ \lambda = \left[ \frac{3D}{c^2 \Delta t} + \frac{1}{2} \right]^{-1}. \]

The collision rule given in equation (7) gives rise to the advection-diffusion equation for solute transport within open-channel flow such that

\[ \frac{\partial C}{\partial t} = \nabla \cdot (D \nabla C - \mathbf{u}C). \]

[20] However, the governing advection-dispersion equation for solute transport through porous media is given by

\[ \phi \frac{\partial C}{\partial t} = \nabla \cdot (D_H \nabla C - \mathbf{v}C) + Q, \]

where \( D_H \) is the hydrodynamic dispersion tensor introduced at the beginning of this section, \( \phi \) is the connected pore fraction, \( \mathbf{v} \) is the Darcy velocity or specific discharge, and \( Q \) is a source or sink of the dissolved solute [e.g., Clauser,
2003]. In the following, we will consider single relaxation time lattice-Boltzmann models which limits the models to the case where \( D_H \) is isotropic and equal to the diffusivity (i.e., \( D_H = D_I \)). This assumption is valid for low Peclet number flows, in which \( D_M \ll D_I \). In that case, equation (11) simplifies to

\[
\phi \frac{\partial C}{\partial t} = \nabla \cdot (\phi D \nabla C - \nu C) + Q. 
\]  

(12)

[21] Nevertheless, the approach presented here can be extended to account for anisotropic dispersion tensors (as required for equation (11)) by adopting a multiple relaxation time lattice-Boltzmann model. Preliminary work outlining such a model is presented in Appendix C. However, as the multiple relaxation time model is more complex than the single relaxation time models, and as here we wish to focus primarily on the question of how to treat heterogeneity in lattice-Boltzmann simulations of solute and heat transfer, we leave the full investigation of a model with anisotropic dispersion for a future publication.

[22] In a homogeneous porous medium with no sources or sinks and transport governed by isotropic dispersion, equation (12) reverts to equation (10) with \( \mathbf{u} \) given by the average pore fluid or seepage velocity, \( \mathbf{u} = \nu \phi \). In this case the standard lattice-Boltzmann advection-diffusion collision rule can be applied. Moreover, this approach can also be used with multiple relaxation time lattice-Boltzmann models [Zhang et al., 2002] to simulate anisotropic dispersion tensors in homogeneous media. However, the \( \mathbf{u} = \nu \phi \) substitution is not applicable for heterogeneous media, as porosity gradients are not correctly accounted for.

[23] The following sections describe two new lattice-Boltzmann models for simulating solute transport through heterogeneous porous media with isotropic dispersion tensors. Model 1, given in section 3.1, delivers the correct governing equations through the addition of a term in the collision rule to correct the temporal concentration derivative. Model 2, given in section 3.2, delivers the correct behavior by decomposing the fluid packets into symmetric and anti-symmetric parts.

### 3.1. Model 1: Collision Term Correction

[24] The model described in this section reproduces the required equation (12) for solute transport in heterogeneous porous media by adding an extra term, \((1 - \phi)g_i(x + \phi \Delta t, t + \Delta t) - g_i(x + \phi \Delta t, t)\), to the collision rule:

\[
\phi g_i(x + \phi \Delta t, t + \Delta t) - g_i(x, t) + (1 - \phi)g_i(x + \phi \Delta t, t) = -\lambda (g_i - g_i^{eq}) + G_i, 
\]  

(13)

where \( G_i \) is the source/sink term for the solute-packets, \( g_i \). As a result of the new term, Model 1 requires an additional 19 multiplication and summation operations per node compared to the standard BGK (Bhatnagar Gross Krook) single-relaxation model [Qian et al., 1992]. The number of memory access operations is also increased by approximately 50% due to the need to read (but not write) the 18 neighboring \( g_i \) values and \( \phi \). The Chapman-Enskog expansion of this collision rule (Appendix A) demonstrates that equation (12) is recovered when the collision frequency and diffusivity are related by

\[
\lambda = \left[ \frac{3D}{C \Delta t} + \frac{1}{2} \right]^{-1}. 
\]  

(14)

and the source/sink term,

\[
\sum_i G_i = Q \Delta t. 
\]  

(15)

The collision frequency, \( \lambda \), and by extension the dispersivity, can vary as a function of space and time. Thus the present model is capable of simulating spatial variations in dispersivity (arising from changes in tortuosity for example) in addition to changes in the porosity.

[25] However, as previously mentioned, it is not possible to simulate anisotropic dispersion with the single relaxation time model. This is because a scalar \( \lambda \) has insufficient degrees of freedom to produce an anisotropic tensor. Nevertheless, this limitation can be overcome by combining the present approach with a multiple relaxation time model. Examples of multiple relaxation-based anisotropic advection-dispersion models for homogeneous media are given by Zhang et al. [2002] and Ginzburg [2005]. We have recently developed our own multiple relaxation time model for heterogeneous media, which is outlined in the preliminary work presented in Appendix C. In Appendix C, we demonstrate that our multiple relaxation time collision rule leads to the correct governing equations for Model 1, and show how to construct the collision matrix, \( \lambda_\nu \), for a given dispersion tensor, \( \mathbf{D}_\nu \). A similar approach can also be applied to introduce anisotropic dispersion tensors in Model 2 and the implicit version of Model 1 discussed below. For simplicity, the remainder of the paper (excluding Appendix C and Figure 9) considers the simplified case where the dispersion tensor is assumed isotropic.

[26] The relationship between the source-sink terms in equation (15) can be satisfied by setting

\[
G_i = w_i Q \Delta t, 
\]  

(16)

which mirrors the approach employed in standard advection-diffusion lattice-Boltzmann models such as those given by Dawson et al. [1993] and Kang et al. [2002b]. For the models presented in this paper, a slight modification of this rule is employed, namely

\[
G_i = \frac{\gamma_i}{C} Q \Delta t. 
\]  

(17)

This approach reduces the possibility of producing negative fluid packet densities in the collision rule, particularly for large \( Q \), and reduces to \( G_i \propto g_i \) to \( Q \propto C \), although it should be noted that the same method is equally applicable to more complex source-sink terms.

[27] Although equation (13) delivers the correct macroscopic behavior, in practice, the collision rule becomes numerically unstable at small connected pore fractions, \( \phi \). As in the standard lattice-Boltzmann model [e.g., Wolf-Gladrow, 2000], linear stability analysis reveals that the new collision rule is conditionally stable in the range \( 0 < \lambda < 2 \), with the most stable value being \( \lambda = 1 \). However, the
presence of $\phi$ in equation (14) implies that as $\phi \to 0$, $\lambda \to 2$, and thus the model becomes unstable at sufficiently low pore fractions even when simulating relatively high solute diffusivities.

[28] The model’s stability is improved with an implicit formulation of the collision rule given in equation (13). Although most lattice-Boltzmann simulations are based on a first-order, forward-difference approximation to the convective derivative, it is equally valid to derive lattice-Boltzmann methods based on implicit (i.e., backward and mixed) difference approximations [e.g., Cao et al., 1997; Lee and Lin, 2003]. For such implicit models, the collision rule is

$$f_i(x + \mathbf{e}_i, t + \Delta t) - f_i(x, t) = \Theta \Omega (x + \mathbf{e}_i, t + \Delta t)$$

$$+ (1 - \Theta) \Omega (x, t),$$

where $\Omega$ is the collision operator, $\Omega = \lambda (f_i^{eq} - f_i)$, and $0 \leq \Theta \leq 1$. When $\Theta = 0$, the standard forward-difference lattice-Boltzmann equations are recovered; $\Theta = 1$ yields a backward-difference approximation; and when $\Theta = 0.5$, a Crank-Nicolson approximation is obtained. While mixed-difference approximations do not alter the convergence properties of hydrodynamic lattice-Boltzmann simulations (forward, backward, and mixed approximations all deliver second-order accuracy), the different methods do affect model stability [Lee and Lin, 2003].

[29] The implicit (backward-difference) version of the solute transport model replaces the collision rule in equation (13) with

$$\phi g_i(x + \mathbf{e}_i, t + \Delta t) - g_i(x, t) + (1 - \phi) g_i(x + \mathbf{e}_i, t + \Delta t)$$

$$= - \lambda [g_i(x + \mathbf{e}_i, t + \Delta t) - g_i^{eq}(x + \mathbf{e}_i, t + \Delta t)]$$

$$+ G_i(x + \mathbf{e}_i, t + \Delta t).$$

This rule contains multiple terms at $t$ and $t + \Delta t$, thus $g_i$ cannot be streamed directly. Instead, the collision rule is rearranged to

$$h_i = \frac{1}{\phi + \lambda}[g_i(x, t) - (1 - \phi) g_i(x + \mathbf{e}_i, t + \Delta t)].$$

From this, the lattice-Boltzmann model is implemented by streaming $h_i$ rather than $g_i$. The value of $g_i(x + \mathbf{e}_i, t + \Delta t)$ is found by first calculating the concentration,

$$C = \frac{\phi + \lambda}{\phi} \sum_i h_i + \frac{Q}{\phi} \Delta t,$$

from which $g_i^{eq}(x + \mathbf{e}_i, t + \Delta t)$, and subsequently $g_i(x + \mathbf{e}_i, t + \Delta t)$, are evaluated.

[30] Changing the convective derivative approximation from a forward to a backward-difference alters the collision-frequency/diffusivity relationship from equation (14) to

$$\lambda = \frac{3 \phi D}{c^2 \Delta t} \left[ \frac{1}{2} \right].$$

The relationship between the collision frequency and the diffusivity for arbitrary values of $\theta$ is given in equation (A13) in Appendix A. Like equation (14), the relationship between $\lambda$ and $D$ is similar to that for a standard, backward-difference model [Lee and Lin, 2003], barring the presence of the pore fraction, $\phi$. Note that $\lambda \to \infty$ as $D\phi \to c^2 \Delta t/6$, implying that the model will become unstable for certain combinations of diffusivities and porosities (as demonstrated later in section 5).

[31] The stability of the simulation can be further improved by normalizing the governing equations by the average connected porosity, $\bar{\phi}$, i.e.,

$$\frac{\partial \bar{\phi}}{\partial t} - \nabla (\bar{\phi} D \nabla C - \bar{\phi} C) + \bar{Q},$$

where $\bar{\phi} = \phi \bar{\phi}$, $\bar{\phi} = \bar{\phi} \bar{\phi}$, and $\bar{Q} = Q/\bar{\phi}$. This approach is only applicable for flows with relatively low fluid velocities, as the adjusted velocity must remain in the low Mach number limit (i.e., $\bar{\phi} \ll c_s$) for the simulation to be accurate.

### 3.2. Model 2: Symmetric/Anti-Symmetric Decomposition

[32] Examining the zeroth- and first-order moments of the equilibrium fluid packets, it is evident that the symmetric and anti-symmetric components represent distinct physical quantities,

$$\sum_i \bar{g}_i^{eq} = \sum_i \bar{g}_i(c_1) = C; \quad \sum_i \bar{g}_i^{eq}(c_1) = 0;$$

$$\sum_i \bar{g}_i^{eq}(c_1) = \sum_i \bar{g}_i^{eq}(c_1) = C V; \quad \sum_i \bar{g}_i^{eq}(c_1) = 0,$$

where subscripted round brackets refer to the symmetric component, $A_i = (A_i + A_i)/2$, and subscripted curly brackets refer to the antisymmetric (or skew) component, $A_i = (A_i - A_i)/2$. Model 2 reproduces the correct constitutive behavior for isotropic dispersion through a porous medium by considering the symmetric and anti-symmetric fluid packet components separately. However, this approach only yields the desired constitutive behavior if a Crank-Nicolson collision rule is employed (i.e., $\theta = 0.5$); as forward or other mixed-difference lattice-Boltzmann collision rules result in the introduction of additional, erroneous terms. Consequently, the collision rule for Model 2 is

$$\phi g_i^{eq}(x + \mathbf{e}_i, t + \Delta t) - \phi g_i^{eq}(x, t)$$

$$+ g_i^{eq}(x + \mathbf{e}_i, t + \Delta t) - g_i^{eq}(x, t)$$

$$= - \frac{\lambda}{2} [g_i^{eq}(x + \mathbf{e}_i, t + \Delta t) - g_i^{eq}(x + \mathbf{e}_i, t + \Delta t)]$$

$$- \frac{\lambda}{2} [g_i^{eq}(x, t) - g_i^{eq}(x, t)] + \frac{1}{2} [G_i^{eq}(x, t) + G_i(x + \mathbf{e}_i, t + \Delta t)],$$

where $\phi_i = \phi(x + \mathbf{e}_i\Delta t/2)$. This pore fraction is set to the average of the two nodes, except when the node at $x + \mathbf{e}_i\Delta t$ is a solid or partial bounce back node, in which case the pore fraction at $x$ is used instead. In the event that $\phi_i = 1$ for all $i$, equation (27) reverts to the Crank-Nicolson form of
As demonstrated in Appendix B, the collision frequency and diffusivity are related in Model 2 by

\[ \lambda = \frac{c^2 \Delta t}{3D}, \tag{28} \]

matching the relationship for Crank-Nicolson-type collision rules given elsewhere [Lee and Lin, 2003; Li et al., 2005]. Thus, unlike Model 1, \( \lambda \) is not a function of pore fraction, \( \phi \), suggesting greater stability for small \( \phi \) (as demonstrated in section 5). As with other Crank-Nicolson-type lattice-Boltzmann models, linear stability analysis suggests the new collision rule is unconditionally stable for all values of \( \lambda \) [Lee and Lin, 2003]. However, it should be noted that this simple stability analysis is not the best indication of the model’s sensitivity to variations in the pore-fraction, or solute concentration gradients.

As in the implicit version of Model 1, \( g_i \) cannot be streamed directly in Model 2 due to the existence of multiple \( t \) and \( t + \Delta t \) terms. Rearranging collision step contributions into terms from current and future time steps results in

\[
\begin{align*}
    h_i &= \phi_i g_i(0)(x,t) + g_i(0)(x,t) - \lambda \left[ \frac{1}{2} [g_i(x,t) - g_i^\prime(x,t)] - \frac{1}{2} G_i(x,t) \right] \\
    h_i &= \phi_i g_i(0)(x + c_i \Delta t, t + \Delta t) + g_i(0)(x + c_i \Delta t, t + \Delta t) \\
    &+ \lambda \left[ [g_i(x + c_i \Delta t, t + \Delta t) - g_i^\prime(x + c_i \Delta t, t + \Delta t)] \\
    &+ \frac{1}{2} G_i(x + c_i \Delta t, t + \Delta t) \right]. \tag{29}
\end{align*}
\]

The values of \( g_i(x + c_i \Delta t, t + \Delta t) \) are calculated from \( h_i \) by first finding the concentration, \( C_i \),

\[
C = \sum_i \left( \frac{[h_i(0) - G_i(0)/2]/A_i}{\sum_i [1 - \lambda B_i(0)/2A_i]} \right), \tag{31}
\]

where \( A_i = \phi_i + \frac{1}{2} \lambda \) and \( B_i = \omega_i [1 + 9(u_i \cdot c_i)^2/2 - 3u_i \cdot u_i] \). Once \( C \) is found, \( g_i(x + c_i \Delta t, t + \Delta t) \) is determined from equation (30). Due to the need to calculate \( h_i \) before and after the streaming step, the computational cost of Model 2 is greater than that of Model 1, requiring slightly more than twice as many multiplication and addition operations compared to the traditional BGK model. The number of memory access operations is increased by approximately 50% as the neighboring \( \phi_i \) values are included in the calculation.

As already mentioned, Model 2 requires the Crank-Nicolson formulation of the collision rule in order to deliver the correct governing behavior, thus additional stability cannot be achieved through either backward, or other forms of mixed-difference approximations. However, stability can still be improved by normalizing the governing equations by a constant, \( \tilde{\phi} \), as discussed for Model 1.

### 4. Simulation of Heat Transport

With some slight modifications, the solute transport models given in the previous sections are capable of simulating heat transport by an incompressible fluid through a porous medium. As with the earlier sections, we consider single-relaxation lattice-Boltzmann models, and hence the effects of anisotropic dispersions are ignored. Buoyancy-driven convection can be modeled in this system, despite the incompressible nature of the fluid, by employing the Boussinesq approximation [Massaioli et al., 1993].

The equations governing heat transport through a porous medium are

\[
(\phi \rho_f C_f + (1 - \phi) \rho_s C_s) \frac{\partial T}{\partial t} = \nabla \cdot (K_m \nabla T - \rho_f C_f \rho_f T_v). \tag{32}
\]

where \( T \) is the fluid temperature, \( C_f \) is the fluid’s specific heat capacity, \( C_s \) is the solid’s specific heat capacity, \( \rho_f \) is the fluid’s specific density, \( \rho_s \) is the solid’s specific density, and \( K_m \) is the mixed thermal conductivity of the fluid-rock composite, which depends on the thermal conductivity of the fluid (\( K_f \approx 0.6\text{Wm}^{-1}\text{K}^{-1} \) for water) and that of the solid (typically \( 1.5\text{Wm}^{-1}\text{K}^{-1} \leq K_s \leq 3\text{Wm}^{-1}\text{K}^{-1} \) for many rocks). For porous media, Sass et al. [1971] report that \( K_m \) is well approximated by the geometric mean, i.e.,

\[
K_m = K_f^{1/2} K_s^{1/2}, \tag{33}
\]

although elsewhere

\[
K_m = \phi K_f + (1 - \phi) K_s \tag{34}
\]

is also given as a low-porosity approximation [Clauser, 2003; Saar and Manga, 2004].

Model 1 and Model 2 are modified to simulate heat flow with the substitutions

\[
\phi \rightarrow \phi + (1 - \phi) \rho_s C_s/\rho_f C_f, \tag{35}
\]

\[
C \rightarrow T, \tag{36}
\]

and setting the collision frequencies to

\[
\lambda = \left[ \frac{3K_m}{\rho_f C_f c^2 \Delta t} \right]^{-1}, \tag{37}
\]

for Model 1 (where addition is employed for the forward-difference model and subtraction for the backward-difference model) and

\[
\lambda = \Delta t (\phi \rho_f C_f + (1 - \phi) \rho_s C_s) / 3K_m \tag{38}
\]

for Model 2. Regardless of the equation used to relate thermal conductivity of the mixed media to that of the solid or the fluid (e.g., equations (33), (34), or (35)), the stability of the two models for heat transport is improved over that for solute transport (demonstrated in section 5) as the collision frequency, \( \lambda \), is no longer as strongly dependent on the porosity.

### 5. Comparison With Analytical and Simulated Results

A series of one-dimensional models, simulating the advection and isotropic dispersion of a constant concentration source, is conducted to assess the accuracy of the three models over a range of velocities and pore fractions. The error between the simulated results and the analytical solution to the one-dimensional advection-dispersion equation [e.g., Batu 2006] is given in Figure 2. Solute transport
through open channels is represented in Figure 2 with a porosity of $\phi = 1$. For diffusivities of $D \sim 1/6 \text{LU}^2 \text{TS}^{-1}$ and porosities $0.5 \leq \phi \leq 1$, the explicit version of Model 1 is in agreement with the analytical solution (Figures 2a and 2d). For $\phi \leq 0.5$ the model becomes unstable and fails to converge. The region of stability is greater for the backward-difference model (Figures 2b and 2e), but still fails to converge at small pore fractions. In addition, the backward-difference model becomes unstable as $\phi D \rightarrow 1/6 \text{LU}^2 \text{TS}^{-1}$ (i.e., $\phi = 1$ in Figure 2b). The greatest stability is shown by Model 2 which is in agreement with the analytical solution for all pore fractions greater than 0.05, given sufficiently low flow velocities (Figures 2c and 2f).

The situation is reversed for heat transport simulations. As expected, the reduced dependence of $l$ to changes in porosity (equation (14)) leads to a greater region of stability for both versions of Model 1 (Figures 3a and 3b). In fact, stable solutions were found for the backward-difference version of Model 1 for the entire range examined, excluding the instability as $\phi K_f/\rho C_f \rightarrow 1/6$ (i.e., $\phi = 1$ in Figure 3b). Conversely, the stability of Model 2 is adversely affected compared to solute transport due to the addition of the pore

Figure 2. Contour plots of the percentage error in solute concentration between the simulated results and analytical solutions for one-dimensional solute advection–dispersion as a function of Darcy velocity, diffusivity, and pore fraction. Results for (a, d) the explicit Model 1, (b, e) the implicit Model 1, and (c, f) Model 2. (top) The error from simulations with a constant diffusivity, $D = 1/6 \text{LU}^2 \text{TS}^{-1}$, as a function of Darcy velocity and pore fraction. (bottom) Error from simulations with a constant Darcy velocity of $0.05 \text{LU} \text{TS}^{-1}$ as a function of diffusivity and pore fraction. Units are given as lattice units (LU) and time steps (TS). Dashed lines given in the top plots indicate the velocity used in the bottom plots. Conversely, dashed lines given in the bottom plots indicate the diffusivity used in the top plots.

Figure 3. Contour plots of the percentage error in temperature between the simulated results and analytical solutions for one-dimensional heat transport as a function of Darcy velocity and pore fraction, with $K/\rho C_f = 1/6 \text{LU}^2 \text{TS}^{-1}$, $K_s = 2 \text{Wm}^{-1} \text{K}^{-1}$, $\rho C_f/\rho C_s = 2.0395$, and $K_m$ given by equation (33) for (a) explicit Model 1, (b) implicit Model 1, and (c) Model 2.
fraction to the expression for \( l \) when heat transport is simulated (Figure 3c).

An analytical solution for the advection and dispersion of solute from a constant-concentration strip source between two impervious boundaries is given by Bruch and Street [1967] and Batu [1989]. In Figure 4, a simulated solution using Model 2 is compared to the analytical solution for a pore fraction of \( \phi = 0.3 \). Excellent agreement was found between the models for velocities and pore fractions within the stable regions indicated in Figures 2c and 2f.

Equally good results are found for simulations that include adsorption reactions of the dissolved solute. This is shown in Figure 5 which compares simulated results from Model 2 to analytical solutions for one- and two-dimensional simulations where the source (positive) and sink (negative) term, \( Q \), in equation (12) is given by

\[
Q = \gamma C,
\]

where \( \gamma \) is a constant of proportionality accounting for adsorption. More complex adsorption reaction equations may also be accommodated by adopting alternate expressions for \( Q \).

To test the new model behavior in systems with heterogeneous porosities and fluid velocities, the simulation was compared to results obtained from the solute transport package of COMSOL, a multiphysics finite element simulator (Figure 6). In this simulation, the flow domain is split into two sections, a higher porosity region on the left of the domain, \( \phi = 0.4 \), and a lower porosity region on the right, \( \phi = 0.1 \). A constant-concentration solute strip source is introduced on the left boundary. Periodic boundary conditions are applied to the top and bottom of the flow domain. A constant flux was applied in both simulations to maintain the same underlying velocity field. Good agreement is again found between solute concentrations for the two simulations, with only a slight discrepancy at the leading edge of the transport front. Similar results are expected for three-dimensional simulations.

6. Example Model Application: Speleogenesis of Carbonate Aquifers

A principle advantage of the new lattice-Boltzmann model presented here, is that it provides the ability to simulate solute and heat transport between open-flow regions (where the flow domain is explicitly described by flow path geometries rather than permeabilities and which are governed by the Navier-Stokes equations) and low-permeability regions (where the flow is described by permeability fields and governed by Darcy’s Law) without requiring remeshing when region boundaries move due to reactions. In this

Figure 4. Overlaid concentration contour plots comparing simulated results from Model 2 (thin black lines) and the analytical solution (thick gray lines) for the advection and dispersion of solute from a constant-concentration strip source between two impervious boundaries. Within the domain \( \phi = 0.3, v = 0.05 \text{ LU/TS}, D = 1/6 \text{ LU}^2/\text{TS}, \) and \( t = 1500 \text{ TS} \). The maximum (input) concentration is normalized to 1, with concentration contours given at intervals of 0.05. Dimensions given in lattice units (LU) and time steps (TS).

Figure 5. Comparison between simulation results from Model 2 and analytical solutions for advection and isotropic dispersion of a solute through porous media with a sink term: \( Q = -\gamma C \), where the constant of proportionality, \( \gamma \), accounts for adsorption. (left) For the one-dimensional simulations, \( \phi = 0.3, v = 0.06 \text{ LU/TS}, D = 1/6 \text{ LU}^2/\text{TS}, \) and \( t = 500 \text{ TS} \), with \( \gamma \) as indicated. (right) For the two-dimensional simulation, \( \phi = 0.3, v = 0.05 \text{ LU/TS}, D = 1/6 \text{ LU}^2/\text{TS}, t = 2000 \text{ TS} \), and \( \gamma = 0.001/\text{TS} \). As in Figure 4, a constant-concentration strip source is considered with an input concentration normalized to 1.
Figure 6. Comparison between Model 2 and COMSOL simulation results for solute transport through a heterogeneous medium with a constant solute strip source, where $\phi = 0.4$ when $x \leq 100$ LU, and where $\phi = 0.1$ when $x > 100$ LU, with $v = 0.068$ LU/TS, $D = 1/6$ LU$^2$/TS, and $t = 4800$ TS. Maximum (influx) concentration is normalized to 1, with concentration contours given at intervals of 0.05.

section, an example of this type of problem is presented, namely the simulation of reactive flow leading to cave formation (speleogenesis) in carbonate aquifers.

Several past papers have employed lattice-Boltzmann techniques to simulate dissolution on small scales where the fluid domain is described explicitly. Kang et al. (2002b) and Verberg and Ladd (2002) used lattice–Boltzmann techniques to simulate chemical dissolution of fractured media. Verhaeghe et al. (2005) demonstrated that lattice–Boltzmann methods reproduce the analytical solution to the classical Stefan moving boundary problem (Stefan, 1889) describing the motion of a dissolving solid boundary (Figure 7).

In the following discussion, we focus on solute transport and a simple disequilibrium-based reaction formulation to highlight the new lattice–Boltzmann method’s capabilities of simulating solute transport through highly heterogeneous systems and its ability to transition seamlessly between open-channel Navier–Stokes flow and porous medium Darcy flow while flow regime boundaries change. More complex reactions and/or heat transport formulations, as introduced in section 4, could easily be implemented as well.

Three active chemical species (components) are modeled in this simulation: (1) the fluid (e.g., water) controlling the advective transport of the other dissolved species; (2) aqueous CO$_2$; and (3) dissolved Ca$^{2+}$ ions. Advective fluid transport within the Darcy flow region is simulated using the partial bounce back model described by Walsh et al. (2009a), while the dissolved phases are simulated using Model 2. Here, we adopt a simplified model in which the rate of dissolution is proportional to the disequilibrium between the local calcium ion concentrations and the equilibrium concentrations. While the reality of natural chemistry is not as straightforward as the simple assumptions adopted in this paper would suggest, our intention in this section is not to present a definitive model of groundwater chemistry, rather we intend to demonstrate the ability of this approach to simulate more complex scenarios than the analytical examples presented earlier. In calculating the rate of dissolution, the lattice–Boltzmann method is first used to find the distribution of the dissolved solutes. As in work by Fredd and Fogler (1998) and Kang et al. (2002b), it is assumed that the dissolution of carbonate is governed by the transfer of reactants and products to and from the calcium carbonate surface, and the reversible surface reaction:

\[
CO_2^{aq} + CaCO_3 + H_2O = Ca^{2+} + 2HCO_3^{-}.
\]

The lattice–Boltzmann simulation is used to find the aqueous carbon dioxide and calcium ion concentrations at the nodes. From this, the equilibrium concentration of dissolved calcium ions is determined using the following empirical relationship, provided by Dreybrodt et al. (2005):

\[
[Ca^{2+}]_{eq} = \left(\frac{p_{CO_2} K_i K_2 H}{4 K_i (\gamma_{Ca}) HCO_3^-}\right)^{1/3} \approx 10.75(1 - 0.0139T)^{3/4} \sqrt{p_{CO_2}} \left(\frac{\mu \text{mol}}{cm^3}\right),
\]

where $K_H$ is the Henry’s constant ($CO_2^{aq} = K_H p_{CO_2}$), $K_1$ and $K_2$ are temperature dependent mass action constants for the dissociation of H$_2$CO$_3$ to HCO$_3^-$ and CO$_2^-$, $p_{CO_2} = p_{CO_2} - [Ca^{2+}]_{eq}/K_H$ is the partial pressure of CO$_2$ prior to any calcium dissolution, and $T$ is the temperature, set to 10°C in the examples considered here. As $p_{CO_2}$ is itself a function of $[Ca^{2+}]_{eq}$, this results in a cubic equation that is solved to find $[Ca^{2+}]_{eq}$. Dissolution rates are determined from the disequilibrium between the local CO$_2$ and calcium ion concentrations, using an empirical relationship by Palmer (1991):

\[
F_s = \begin{cases} 
 k_{n1} (1 - C/C_{eq})^{n_1} & \text{for } C \leq C_s \\
 k_{n2} (1 - C/C_{eq})^{n_2} & \text{for } C > C_s 
\end{cases}
\]

where $C$ is the calcium concentration, $C_{eq}$ is the equilibrium concentration, $C_s$ is the switch concentration, and $k_{n1}, k_{n2}, n_1,$ and $n_2$ are temperature dependent mass action constants for the reversible surface reaction.

Figure 7. Comparison between the analytical solution to the classical Stefan moving boundary problem (Stefan, 1889), and simulated results from the lattice–Boltzmann model originally developed by Verhaeghe et al. (2005).
and $n_2$ are empirical constants. Although only solid dissolution is considered in this paper, mineral precipitation reactions might also be accommodated in the same manner by using the same approach to increase, rather than decrease, the local solid fraction. It is worth noting that the reversibility of dissolution/precipitation reactions is highly uncertain [Steefel and Cappellen, 1990; Xu et al., 2005]. However, more complex and differing dissolution/precipitation reactions can be substituted for the simple reaction laws used here.

The initial fluid flow domain is represented as a lattice of randomly distributed solid fractions, $1 - \phi$, between 0.0 and 1.0. For this simple example, the permeability-porosity relationship at each node matches that used by Thorne and Sukop [2004] and Walsh et al. [2008], i.e., the parameter $\alpha$, given in equation (5), is assumed equal to the solid fraction. Initially, the dissolved ions within the system are set to an equilibrium concentration of 2.746 mmol for the calcium ions and a partial pressure of 0.02611 atm for the aqueous carbon dioxide. The influx values are set to 2.6 mmol for the calcium ions and 0.03 atm for the aqueous carbon dioxide.

The growth of the simulated cave system is shown in Figure 8. The Reynolds numbers calculated from the maximum flow velocity and channel width at that point, is 0.7 in the top row, 8.9 in the middle row, and 16.5 in the bottom row of Figure 8, suggesting predominantly laminar flow. This example demonstrates the model’s ability to simulate flow through a wide range of material permeabilities and complex flow regions, and handle moving boundaries with a single model that does not require remeshing of the flow field as would be required in a finite element model. These abilities have important applications outside of solute transport simulations. For example, the heat transport formulation of the model has applications in large-scale geological problems such as simulations of glacial melting, partial melt flows in magmatic systems, or geothermal energy recovery. Furthermore, due to the relative ease with which a wide range of chemically and biologically mediated reactions can be incorporated into these multiphase, multicomponent fluid and heat transport lattice-Boltzmann simulations, the discussed methods can be readily adapted to many fields in science and engineering.

7. Conclusions

Standard lattice-Boltzmann methods provide a means to model fluid flow in a known domain geometry. More recently, modified lattice-Boltzmann methods have been developed based on a macroscopically averaged description of the fluid flow, thereby allowing large-scale simulations of fluid flow through heterogeneous porous media. A key advantage of these lattice-Boltzmann models is their ability to handle complex and changing boundary conditions, as well as interpolate between fluid flow behaviors ranging from open channel (Navier-Stokes) to porous medium...
(Darcy’s Law) flow. Macroscopic lattice-Boltzmann models have also been introduced to simulate solute and heat transport, however these models have been unable to simulate transport through heterogeneous media.

[50] Here we have presented two new lattice-Boltzmann methods that now allow large-scale macroscopic modeling of solute and heat transport through heterogeneous media. The first method adjusts the macroscopic constitutive behavior by modifying the standard lattice-Boltzmann collision rule to correct the temporal derivative of the solute advection-dispersion equation. The second method decomposes the fluid packet contributions into symmetric and anti-symmetric components and weights the rate of relaxation of those components separately. As a simplifying assumption, we have considered single relaxation time lattice-Boltzmann models. This restricts the simulations to problems with isotropic dispersion tensors as may be assumed in low Peclet number flows. Nevertheless, by employing a multiple relaxation time approach both methods can be extended to include anisotropic dispersion tensors, as shown in preliminary work presented in Appendix C. A full analysis of the stability and accuracy of such anisotropic models is the subject of ongoing research.

[51] Both of the new methods for modeling solute and heat transport deliver the desired macroscopic constitutive behavior (under the assumption of isotropic dispersion), as demonstrated by Chapman-Enskog expansions of the governing equations (the same is also demonstrated for the anisotropic multiple relaxation time model in Appendix C). However, in practice the models become numerically unstable when simulating flows through low-porosity regions. The stability of Model 1 (section 3.1) is improved by employing an implicit formulation of the model based on a backward-difference approximation to the convective derivative. However, this method cannot be applied to Model 2 (section 3.2), which necessarily uses a Crank-Nicolson approximation. An alternative method for improving the stability of both models in low velocity flows, is to normalize the model by the mean porosity.

[52] The accuracy of the new models was evaluated by comparing their predictions to analytical and simulated solutions for solute and heat transport through porous media. Excellent agreement is found between the new models and one- and two-dimensional analytical solutions for advection and isotropic dispersion through a homogeneous porous medium, as well as for one- and two-dimensional simulations of reactive transport. Equally good results are obtained when comparing the new simulation with results from the finite element simulator COMSOL for solute transport in a heterogeneous medium. Finally, the ability of the new model to simulate transport through materials with a wide range of permeabilities was demonstrated by formulating a toy reactive flow model of speleogenesis in a carbonate system, which simulates cave development in response to the influx of a disequilibrium calcium-ion/aqueous-CO$_2$ solution.

Appendix A: Chapman-Enskog Expansion of Model 1

[53] In this appendix, the Chapman-Enskog expansion is applied to the collision rule for Model 1 (equation (13) and reproduced below) to show that the correct governing behavior for porous media solute transport with an isotropic dispersion tensor (equation (12)) is recovered in the macroscopic limit. The approach used is based on that given by Dawson et al. [1993] and Banda et al. [2008].

[54] The collision rule is

$$
(1 - \alpha)g_i(x + c_i \Delta t, t + \Delta t) - g_i(x, t) + \alpha g_i(x + c_i \Delta t, t)
$$

$$
= (1 - \theta)\left[ G_i(x, t) - \lambda g_i(x, t) - g_i^{eq}(x, t) \right] + \theta \left[ G_i(x + c_i \Delta t, t + \Delta t) - \lambda g_i(x + c_i \Delta t, t + \Delta t) - g_i^{eq}(x + c_i \Delta t, t + \Delta t) \right].
$$

(A1)

The left-hand side of this collision rule contains an additional term, $\alpha (g_i(x + c_i \Delta t, t) - g_i(x + c_i \Delta t, t + \Delta t))$, absent from the standard single relaxation time collision rule, which ultimately accounts for the difference between the temporal derivative in the advection isotropic-dispersion equation for porous medium flows compared to the standard advection-diffusion equation. Note that, although $\lambda$ is a constant in the standard lattice-Boltzmann simulation (equation (9)), it need not be and is assumed to vary both as a function of position and time.

[55] Expanding both sides of equation (A1) as a second-order Taylor series gives

$$
D_i \frac{\Delta t}{2} g_i^{eq} - \frac{\partial g_i}{\partial t} - \frac{\Delta t}{2} \frac{\partial^2 g_i}{\partial t^2} = -\lambda \frac{\Delta t}{2} \left[ g_i^{eq} - g_i^{eq}(x - \theta \Delta t) \right] + \frac{G_i}{\Delta t},
$$

(A2)

where $D_i = \frac{\partial^2}{\partial x^2} + c_i \cdot \nabla$ is the convective derivative.

[56] The solute packets, $g_i$, are then expressed as asymptotic expansions about the equilibrium distribution, $g_i^{eq}$, in terms of a small parameter, $\varepsilon$:

$$
g_i = g_i^{eq} + \varepsilon g_i^{(1)} + \varepsilon^2 g_i^{(2)},
$$

(A3)

such that $g_i^{(0)} = g_i^{eq}$ and hence $\sum g_i^{(m)} = 0$ for $m > 0$. In addition, two timescales ($t_1 = \varepsilon t$ and $t_2 = \varepsilon^2 t$), and a length scale ($x_1 = \varepsilon x$) are introduced, yielding

$$
\frac{\partial}{\partial t} = \varepsilon \frac{\partial}{\partial t_1} + \varepsilon^2 \frac{\partial}{\partial t_2},
$$

(A4)

$$
\nabla = \varepsilon \nabla_1.
$$

(A5)

Written in terms of the asymptotic expansion, and the two time and length scales, equation (A2) becomes

$$
\varepsilon D_{1i} g_i^{(0)} + \varepsilon^2 \left( D_{2i} g_i^{(1)} + \frac{\partial g_i^{(0)}}{\partial t_1} + \frac{\Delta t}{2} D_{1i}^2 g_i^{(0)} \right)
$$

$$
- \varepsilon \alpha \frac{\partial g_i^{(0)}}{\partial t_1} - \varepsilon^2 \alpha \left( \frac{\partial g_i^{(1)}}{\partial t_1} + \frac{\partial g_i^{(0)}}{\partial t_2} + \frac{\partial \Delta t}{\partial t_1} g_i^{(2)} \right)
$$

$$
= \lambda \left[ g_i^{(1)} + \varepsilon \theta \Delta t D_{1i} g_i^{(1)} + \varepsilon^2 g_i^{(2)} \right] + \varepsilon^2 \frac{G_i^{eq}}{\Delta t},
$$

(A6)

where $D_{1i} = \frac{\partial}{\partial x_1} + c_i \cdot \nabla_1$. Equating first-order terms from equation (A6)

$$
D_{1i} g_i^{(0)} - \frac{\partial g_i^{(0)}}{\partial t_1} = \lambda \frac{G_i^{eq}}{\Delta t},
$$

(A7)
and summing over lattice directions, \( c_i \),

\[
(1 - \alpha) \frac{\partial C}{\partial t_1} + \nabla_1 \cdot (C v) = 0 .
\] (A8)

Taking the velocity moments of the first-order terms, i.e., taking the product with \( c_i \) and again summing over lattice directions,

\[
(1 - \alpha) \frac{\partial (C v)}{\partial t_1} + \frac{c^2}{3} \nabla_1 C = -\lambda \frac{\Delta t}{\Delta t} \Pi^{(1)},
\] (A9)

where \( \Pi^{(1)} = \sum_i g_i^{(1)} c_i \). Finally, equating second-order terms from equation (A6),

\[
\nabla_1 \cdot \left[ \left( 1 - \theta \right) g_i^{(1)} c_i \right] + (1 - \alpha - \lambda \theta) \frac{\partial g_i^{(1)}}{\partial t_1} + \frac{\partial^2 g_i^{(1)}}{\partial t_2} + \frac{\Delta t}{2} \nabla_1 \cdot \left[ c_i \alpha \frac{\partial g_i^{(1)}}{\partial t_1} \right] = -\lambda \frac{\Delta t}{\Delta t} \Pi^{(2)} + G_i^{(2)} .
\] (A10)

[57] Combining equations (A9) and (A10), and assuming the velocity, \( v \), is small compared to the lattice speed, \( c \) (i.e., assuming that the model is operating in the low Mach number limit, a necessary condition for lattice-Boltzmann models in general [Wolf-Gladrow, 2000]), provides

\[
(1 - \alpha) \frac{\partial C}{\partial t_2} - \nabla_1 \cdot \left[ \left( 1 - \frac{1}{\lambda} + \theta \right) \frac{c^2 \Delta t}{3} \nabla_1 C \right] = \frac{1}{\Delta t} \sum_i G_i^{(2)} .
\] (A11)

Then, by adding equations (A8) and (A11),

\[
(1 - \alpha) \frac{\partial C}{\partial t} + \nabla \cdot (C v) = \nabla \cdot \left[ \left( 1 - \frac{1}{\lambda} + \theta \right) \frac{c^2 \Delta t}{3} \nabla C \right] + Q ,
\] (A12)

where \( Q = \sum_i G_i / \Delta t \). This expression is equivalent to equation (12) if the collision frequency, \( \lambda \), is given by

\[
\lambda = \left[ 3 \frac{\phi D}{c^2 \Delta t} + 1 - \theta \right]^{-1} .
\] (A13)

and

\[
\alpha = 1 - \phi ,
\] (A14)

i.e., \( \alpha \) is the solid fraction.

**Appendix B: Chapman-Enskog Expansion of Model 2**

[58] In this appendix the Chapman-Enskog expansion is applied to Model 2, given in section 3.2. With a change of reference frame, the Crank-Nicolson form of the collision rule given in equation (27) is expressed as

\[
\phi g_i(x + c_i \Delta t, t + \Delta t) - g_i(x, t) + (1 - \phi) g_i(x + c_i \Delta t, t + \Delta t) = \Omega(x, t) ,
\] (B1)

which, expanded as a second-order Taylor series, becomes

\[
\Delta t \left[ \phi D g_i(x) + D g_i(x) \right] = \Omega(x, t) .
\] (B2)

[59] Introducing the asymptotic expansion, results in

\[
\phi \left[ \epsilon D g_i^{(0)} + \epsilon^2 D g_i^{(1)} + \epsilon^3 \frac{\partial g_i^{(0)}}{\partial t_2} \right] + \epsilon D g_i^{(0)} + \epsilon^2 D g_i^{(1)} + \epsilon^3 \frac{\partial g_i^{(0)}}{\partial t_2} = -\lambda \frac{\Delta t}{\Delta t} \left( c_i^{(1)} - \epsilon^2 g_i^{(2)} \right) + \epsilon^2 \frac{\Delta t}{\Delta t} .
\] (B3)

Collecting terms to first-order and summing gives

\[
\phi \frac{c^2}{3} \nabla_1 \cdot (c^3 \nabla C) + \frac{\partial C}{\partial t_1} = -\lambda \frac{\Delta t}{\Delta t} \Pi^{(1)} .
\] (B5)

[60] Likewise, collecting the second-order terms and summing yields

\[
\frac{\partial C}{\partial t_2} - \nabla_1 \cdot \left( \frac{\phi c^2 \Delta t}{3 \lambda} \nabla C - \nabla v C \right) = Q .
\] (B6)

Combining the first- and second-order results gives

\[
\phi \frac{c^2}{3} \nabla_1 \cdot (c^3 \nabla C - \nabla v C) + Q ,
\] (B7)

which delivers the correct constitutive behavior for equation (12) when the collision frequency is given as \( \lambda = \frac{c^2 \Delta t}{\Delta t} \).

**Appendix C: Anisotropic Dispersion Tensor**

[61] The single-relaxation (scalar-\( \lambda \)) lattice-Boltzmann models presented in this paper are unable to represent the anisotropic hydrodynamic dispersion tensor in equation (11). However, this problem can be overcome by adopting a multiple relaxation time model where the collision frequency is no-longer scalar but instead a second-rank tensor, \( \lambda_{ij} \). Here, we adopt a slightly different approach from the multiple relaxation time models for homogeneous media mentioned in the main text [Zhang et al., 2002; Ginzburg, 2005], and instead replace the single-relaxation collision rule given in equation (13) with

\[
\phi g_i(x + c_i \Delta t, t + \Delta t) - g_i(x, t) + (1 - \phi) g_i(x + c_i \Delta t, t + \Delta t) = \Omega(x, t) ,
\] (B1)

\[
\begin{align*}
\Phi g_i(x + c_i \Delta t, t + \Delta t) - g_i(x, t) + (1 - \phi) g_i(x + c_i \Delta t, t + \Delta t) = & \Omega(x, t) , \\
& \text{for } i = 1, \ldots, M
\end{align*}
\] (C1)
which results in the desired governing equation if

$$\Lambda = \left[ \frac{3\phi}{c^2\Delta t} \mathbf{D_H} + \left( \frac{1}{2} - \theta \right) \mathbf{I} \right]^{-1}. \quad (C8)$$

There are multiple ways to define $\lambda_j$ to meet the conditions in equations (C2) and (C3). Here, $\lambda_j$ is given in matrix form as

$$\lambda = \mathbf{c}^T \left( \mathbf{e}^T \right)^{-1} \mathbf{A} \mathbf{c} + \frac{\text{Tr}(\mathbf{A})}{3} \Omega, \quad (C9)$$

where (with a slight abuse of notation) $\mathbf{c}$ is taken to represent a $3 \times 19$ matrix of lattice velocities, i.e., $\mathbf{c} = [c_1, c_2 \ldots c_{19}]$. $\text{Tr}(\mathbf{A})$ is the trace of the matrix $\mathbf{A}$, i.e., $\text{Tr}(\mathbf{A}) = \lambda_{11} + \lambda_{22} + \lambda_{33}$ and $\Omega$ is a $19 \times 19$ matrix given by

$$\Omega = \mathbf{I} - \mathbf{e}^T \left( \mathbf{e}^T \right)^{-1} \mathbf{c}. \quad (C10)$$

An advantage of this definition over other possible expressions for $\lambda_j$ is that the inverse, $\lambda_j^{-1}$ (required for Model 2 and implicit versions of Model 1) has a simple analytical expression:

$$\lambda^{-1} = \mathbf{c}^T \left( \mathbf{e}^T \right)^{-1} \mathbf{A}^{-1} \mathbf{c} + \frac{3}{\text{Tr}(\mathbf{A})} \Omega. \quad (C11)$$

[66] The model’s ability to simulate anisotropic dispersion is demonstrated in Figure 9. In this example, the principle directions of the dispersion tensor are not aligned with the grid and the eigenvalues of the dispersion tensor differ by two orders of magnitude. Despite these complicating conditions the simulation shows good agreement with the analytical solution.

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