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Direct simulation of the influence of the pore structure on the diffusion process in porous media

Yumei Yong [a], Xiaojun Lou [a], Sha Li [a], Chao Yang [a,*], Xiaolong Yin [b]

[a] Key Laboratory of Green Process and Engineering, Institute of Process Engineering, Chinese Academy of Sciences, Beijing 100190, China
[b] Petroleum Engineering Department, Colorado School of Mines, Golden, CO 80402, USA

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ABSTRACT

In this paper, we numerically study the influence of pore structures on diffusion processes in porous media. The porous media geometry models are constructed based on two-dimensional Voronoi diagrams, and they feature randomly connected channels with large pores embedded to simulate the heterogeneity of porous media. A link-type two-relaxation-time (LTRT) lattice Boltzmann (LB) method is employed to solve the diffusion equation. The tortuosity is characterized as a function of porosity and pore structure. From numerical results, a correlation for the tortuosity as a function of porosity is derived for Voronoi geometries without large pores. Geometries with large pores at the same total porosity have higher tortuosity, which indicates that geometric heterogeneity slows down the diffusion.

1. Introduction

Porous media are ubiquitous. Understanding and control of the flow and transport properties of porous media are important for the design of chemical reaction processes such as combustion, pyrolysis, and catalysis. Based on the IUPAC notation [1], porous materials should be classified as *macroporous* if the pore diameters are larger than 50 nm, as *microporous* if the pore diameters are less than 2 nm, and as *mesoporous* if the pore diameters fall between 2 and 50 nm. For mesoporous and microporous materials, because the characteristic pore size severely limits advection, diffusion is usually the dominant transport mechanism. A detailed understanding of diffusion processes in porous media is thus crucial. The use of Fick's first law to model diffusion fluxes is arguably the most common and important method. If the diffusing species does not interact with the porous solid, the rate of diffusion is a function of the pore structure. The pore structure generated by Voronoi diagrams [2,3] is a physical realization of the conceptual porous media model based on random networks of channels. In this study, we use a lattice Boltzmann method to directly solve the diffusion equation in two-dimensional (2D) porous media based on Voronoi diagrams, and present the effective diffusion as a function of porosity and pore structure.

In a porous medium, the presence of solid phase causes the diffusion paths of species to deviate from straight lines. To represent the role of pore structures on diffusion, the diffusion coefficient is often scaled with tortuosity $\tau^2 = D_m/D_e$, where τ is the tortuosity, D_m is the diffusion coefficient of the species of interest in bulk pore fluid, and D_e is the effective diffusion in porous media [4,5]. Note that the tortuosity is always tied to the effective length traveled by a flux, and therefore its definition is not unique [6]. The tortuosity in this study is defined for diffusion through porous media. Attempts have been made to incorporate tortuosity using experimental [7], theoretical [8], and empirical approaches [9].

* Corresponding author.
E-mail address: chaoyang@home.ipe.ac.cn (C. Yang).

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Analytical approaches to relate the effective diffusivity and structural properties of porous media have often been developed based on mathematically idealized geometries (e.g., spherical or rectangular packings). For complicated random pore geometries, it is difficult to use experimentally measured effective diffusion coefficients to isolate the effect of geometry, because the coefficients can be affected by the interaction (e.g., adsorption) between the diffusing species and the porous medium. The reported adjustable parameters in the diffusion coefficient often vary significantly [4]. Numerical determination of the effective diffusion coefficient, in contrast, allows one to isolate the effect of pore geometry.

More recently, the advance in scientific computing has allowed development of a number of studies to analyze the influence of complex porous structures on mass transport mechanisms. Basically, two main approaches have been used to produce the pore geometry. The first approach considers a porous medium composed of network sponges and inter-connected microchannels [10]. The second approach considers the detailed geometry of a given porous medium, which can be periodically or randomly arranged "particles" of various shapes [11], or directly from scanned images of a real porous medium [12].

In many cases, researchers have tried to extract from computer simulations the relation between porosity and the normalized effective diffusivity or tortuosity, because such relations are apparently very useful for predictive purposes. Although it is impossible to have a general formula that is able to quantitatively predict the effective diffusivity from the porosity for all porous media, for porous media with idealized structures, such correlations may be established. Among others, Kim and Chen [13] evaluated the tortuosities of both regular structures, including simple cubic (SC), face-centered and body-centered cubic (FCC and BCC), and random structures of mono-dispersed spherical particles by Monte Carlo simulations. Hizi and Bergman [14] used the Fourier approach of Dunn and Bergman [15] to evaluate the effective diffusivity and tortuosity in simple cubic arrays of overlapping mono-dispersed octahedral elements. Quintard and Whitaker [16] studied the rectangular and elliptical obstacles in SC and FCC arrangements using the method of volume averaging. In the work of Caravella et al. [17], a number of unit cells were assembled along the diffusion direction without additional space to simulate the effect of the bi-dispersivity of the particle size on the tortuosity of three-dimensional porous media. In natural porous media, some solid grains may be lost in the diagenesis process, leading to large and isolated pores. The existence of large pores will lead to different transport properties of pore media, so it is necessary to study its effect on diffusion. There are few papers that numerically explore the rules of pore structure and diffusion in porous media with large and isolated pores. In our study, we use Voronoi diagrams to generate structures with large pores separated by channels by randomly subtracting grains, and we characterize the differences in the effective diffusion from porous media models based on a random network.

In this paper, we use pore-scale numerical simulation to study the influence of the pore structure on the diffusion process in porous media. First, a link-type two-relaxation-time (LTRT) lattice Boltzmann (LB) model and the method to generate porous media models composed of large pores and channels based on the Voronoi tessellation are introduced. Then, we verify the LTRT model. Subsequently, on the pore scale, we directly solve the diffusion equation in porous media produced randomly with different diameter channels, seed numbers, and fractions of channels and large pores. By analyzing the numerical results, we present a formula relating the tortuosity and porosity.

2. Mathematical model

Pore-scale direct numerical simulation of diffusion can be a simulation of the random walk process [18–20] or a direct solution of the diffusion equation [21]. The Lattice Boltzmann (LB) method is popular for porous media applications due to its simplicity in handling complex geometries [22–24]. Therefore we use an LB method to directly solve the diffusion equation in porous media composed of randomly distributed channels and large pores to explore the effect of pore structure on diffusion processes.

In this study, the LTRT lattice Boltzmann model, developed to solve the full advection–diffusion equations, is applied to solve the diffusion equation in porous media. Besides solving the fluid dynamics equation, the lattice Boltzmann method can also be used to solve advection–diffusion equations [25–27]. The LTRT lattice Boltzmann model, developed by Ginzburg [28,29], is one of the existing approaches that extend the lattice Boltzmann method to the advection–diffusion problem; it has the characteristics of higher accuracy, less computational load, higher stability, and simpler programming. The LTRT model coincides with one particular eigenvalue configuration, and the two-relaxation-time collision operator is suitable for both mass and momentum conservation laws. The two-relaxation-time operator is equivalent to the Bhatnagar–Gross–Krook (BGK) collision in simplicity, but the additional collision freedom relates it to multiple-relaxation-time (MRT) models. The "optimal convection" and "optimal diffusion" eigenvalue solutions for the LTRT model allow removal of next-order corrections to advection and anisotropic-dispersion equations. Our implementation of the LTRT model is two dimensional, and we will present the main model equations below. First, the LTRT discrete Boltzmann equation is

$$f_i(\boldsymbol{x}+\boldsymbol{c}_i\delta t, t+\delta t) = f_i(\boldsymbol{x}, t) - \frac{1}{\tau_s}(f_i^s(\boldsymbol{x}, t) - f_i^{\mathrm{seq}}(\boldsymbol{x}, t)) - \frac{1}{\tau_\alpha}(f_i^a(\boldsymbol{x}, t) - f_i^{\mathrm{aeq}}(\boldsymbol{x}, t)), \tag{1}$$

where $f_i(\boldsymbol{x}+\boldsymbol{c}_i\delta t, t+\delta t)$ represents the post-collision particle distribution function at (x, t) streamed to the neighboring nodes located at $(\boldsymbol{x}+\boldsymbol{c}_i\delta t)$ and at time $t+\delta t$ along direction i, $f_i(\boldsymbol{x}, t)$ is the pre-collision particle distribution function, $f_i^s(x, t)$ and $f_i^{\mathrm{seq}}(x, t)$ are the symmetric parts of the distribution function $f_i(x, t)$ and the equilibrium distribution function $f_i^{\mathrm{eq}}(x, t)$, and $f_i^a(x, t)$ and $f_i^{\mathrm{aeq}}(x, t)$ are respectively the anti-symmetric part of the distribution function $f_i(x, t)$ and the equilibrium distribution function $f_i^{\mathrm{eq}}(x, t)$. Eq. (1) indicates that the distribution functions of particles reach the equilibrium state by