Molecular dynamics simulations of oil transport through inorganic nanopores in shale

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HIGHLIGHTS

- This work is the first study of oil flow through inorganic nanopores in shale.
- We present two methods to correct liquid flow: slip length and apparent viscosity.
- Slip length is exponentially dependent on driving force, pore size, and temperature.
- Neglecting the interfacial slip under-predicts liquid flow rate.
- Calculated slip can be readily used into existing tools to get liquid permeability.

GRAPHICAL ABSTRACT
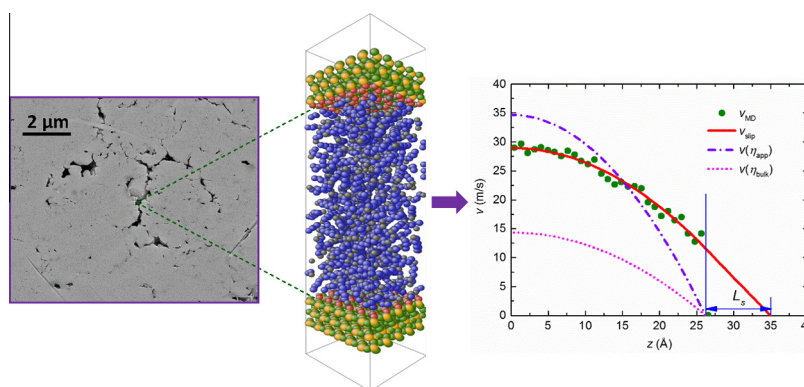
ARTICLE INFO

ABSTRACT

Understanding the transport of liquid hydrocarbon through nanopores of inorganic minerals is crucial not only to develop liquid-rich shale reservoirs, but also to grasp oil migration from deeply buried extremely low permeability source rocks. We report a molecular study of liquid hydrocarbon (octane) flow through inorganic (quartz) nanopores ranging in size from 1.7 to 11.2 nm. Through equilibrium molecular dynamics (EMD), we observe the layering structure of confined octane and conclude that in the center of slits having apertures greater than 3.6 nm, the octane properties, e.g., density, self-diffusion coefficient, and viscosity, tend to be bulk-liquid-like. Near the solid–liquid interface, octane molecules diffuse more slowly. Then we use nonequilibrium molecular dynamics (NEMD) to study the pressure-driven flow of octane in quartz slits and present two methods to characterize the behavior: (1) slip length coupled with effective viscosity and (2) apparent viscosity. The Navier–Stokes equation can reasonably describe the flow in quartz nanopores larger than 1.7 nm; however, a slip boundary condition or viscosity correction is essential. Although the slip length (∼0.9 nm) is small, significant error can be caused in the estimation of overall flux if it is neglected. The variations in slip length and apparent viscosity with driving force, pore size, and temperature can be described by empirical exponential functions. These results can be readily incorporated into existing techniques to estimate apparent liquid permeability of shale—the most fundamental property required for shale exploitation.

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1. Introduction

Because of its large reserves and considerable production rate after fracking, shale, once considered only as the source rock of fossil fuels for its widespread nanopores and extremely low permeability, is changing the game throughout the global energy industry, thus leading to a worldwide "shale revolution" [1]. As one of the most significant innovations in petroleum history, shale development not only alleviates the impending energy crisis, but also shows great potential to reduce carbon dioxide emissions [2,3]. Driven by the tremendous economic benefits and political interests, many nations and areas—including the U.S., Canada, China, Australia, and most European countries—have started strong programs to explore and develop hydrocarbons stored in shale [4]. Although significant progress has been achieved in the corresponding equipment and technologies, the intrinsic complexity of shale has restricted an understanding of the fluid transport behavior [3,5]. As the cornerstone of mathematical descriptions at the Darcy scale and field scale, the science of mass transfer through nanoporous material is essential for developing numerical simulation, production optimization, and asset evaluation of shale resources. Thus, a new branch of subterranean hydrodynamics has emerged [4].

Characterization of shale pore structure using atomic force microscopy (AFM) and scanning electron microscopy (SEM) has yielded insight into the universal occurrence of complex multiscale pore networks in shales. The pores range in size from micrometers to nanometers (2–100 nm) [6,7]. For the two largest shale oil plays in the U.S., Bakken and Eagle Ford, the most frequent pore radii are estimated to be 19 and 8.5 nm, respectively [8,9]. X-ray diffraction (XRD) mineralogy analysis reveals that shales are typically composed of variable amounts of organic matter (kerogen, bitumen) and inorganic minerals, like quartz, dolomite, and calcite, as well as clays [5,7]. Among these components, quartz is thought to play a significant role because its brittleness is favorable for fracture propagation—this is one of the prerequisites for higher production rate [10]. In Fig. 1, we present an SEM image of an ion-milled Woodford shale sample exemplifying pores among quartz crystals representing inorganic material.
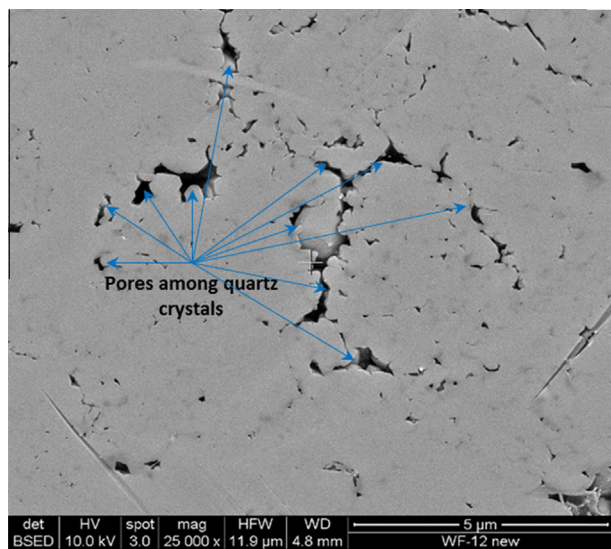

Fig. 1. SEM image of an ion-milled Woodford chert sample, composed of 90% quartz, with minor amount of organic matter, clay minerals, and carbonate. The TOC content is about 2.44 wt% in this sample, with *Tmax* = 447 °C. This indicates the sample is already mature and underwent certain amount of oil generation.

The transport behavior of gaseous methane through silica and carbon-based materials has been the focus of numerous studies, ranging from the nanoscale by molecular dynamics (MD) [11–13] to the Darcy scale using bench experiments [14], analytical mathematical models [4,6], and the lattice Boltzmann method (LBM) [15], among others. The pressure-driven flow of liquid hydrocarbons in shale inorganic nanopores, however, remains unexplored. Two important applications include oil migration from deeply buried ultralow permeability source rocks [16,17] and oil/gas condensate production from liquid-rich shale reservoirs [3,4,18]. In the present work, we concentrate on the transport of liquid alkanes through quartz nanopores because quartz is the major component in the pore networks of the shale matrix [5,7,10]. Understanding how liquid flows through nanoporous materials not only provides a basis for the effective exploitation of shale resources but also may shed light on a wide range of natural science and industrial applications, e.g., sequestration of carbon dioxide and nuclear waste in geologic repositories [19], gas separation and liquid purification with highly selective membranes [20], and the design of micro-/nano energy conversion machines [21].

Quartz has attracted the attention of researchers in many disciplines, like the geosciences [22,23], biophysics [24,25], and microfabrication [26]. However, most of the existing research primarily addresses the structures and properties of the quartz–water interface [22,23,27,28]; only a few documented studies are associated with the oil–silica system. Using infrared (IR)-visible sum-frequency generation (SFG) vibrational spectroscopy, Yang et al. [29] found that compared with *n*-alkanes, toluene shows a stronger preference for adsorption on silica. They also observed that toluene molecules distribute asymmetrically on the interface with a tilting angle of 25°, whereas *n*-alkane molecules adopt a predominantly parallel orientation. Ledyastuti et al. [30] validated this conclusion with MD simulations of toluene and heptane on both hydrophobic and hydrophilic surfaces of quartz. Chilukoti et al. [31] reported that liquid alkanes are more favorable to adsorb on the $(0\,0\,1)$ surface of α-quartz, and these molecules tend to lie parallel to this interface over $(0\,1\,1)$ and $(1\,0\,0)$ crystal planes. On the basis of the quantum density functional theory (DFT), Hantal et al. [5] studied the energetically favorable chemical bond between kerogen and silica, examined the performance of the reactive force field (ReaxFF), and proposed a method for the atomic-scale reconstruction of the interface. Later, Le et al. [32] simulated the adsorption isotherm, molecular structure, and self-diffusion coefficient of propane confined in a silica slit via MD. Their results are in qualitative agreement with those of earlier experiments. They also observed layering of propane molecules at the near-wall region. Nevertheless, we cannot find any publications on the pressure-driven flow behavior of liquid alkanes in quartz nanopores. According to our knowledge, this work is the first attempt to explore such a significant topic.

Here, we present an MD simulation study of *n*-octane flow through quartz nanoslits composed of two identical $(1\,0\,\bar{1}\,0)$ crystal planes. Using equilibrium molecular dynamics (EMD), we analyzed the molecular structure and diffusion property of *n*-octane confined in slits having apertures ranging from 1.7 to 11.2 nm. Then the velocity profile, fluid viscosity, and slip length were calculated via nonequilibrium molecular dynamics (NEMD). We examined the effects of driving force, pore size, and temperature on the hydrodynamics behavior of confined alkane. Most precisely, this study will answer the following questions: (1) What is the difference between hydrocarbon properties in confined quartz nanopores and those in bulk? (2) Can the velocity profile be accurately characterized by the Navier–Stokes equation coupled with the slip boundary condition? (3) Can quantitative predictions of nanoconfined flow behavior be made using apparent viscosity instead of the bulk value?