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Study of transport of fluids under nano-confinement using non-equilibrium molecular simulation

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for the degree of Doctor of Philosophy

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Declaration of Originality

I, Weilun Xu, hereby declare that the work in this thesis is my own and that work from others has been referenced appropriately.

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Abstract

The boundary-driven non-equilibrium molecular dynamics (BD-NEMD) has been introduced to evaluate the mass transport coefficients of fluids in nano-confinement. In contrast to the traditional equilibrium simulation route, BD-NEMD directly measures flux and thermodynamic gradients between upstream and downstream of a porous media, which leads to accurate transport parameters while demanding less computational cost. In this work, the use of BD-NEMD on nano-confined fluids are investigated and extended to binary fluids. A novel technique that evaluates steady-state adsorbed densities at pore entry/exit using adsorption isotherms is proposed. By comparing with the traditional EMD method, it is shown that BD-NEMD is robust and suitable for the study of the transport of dense fluids in nano-confinement.

BD-NEMD is further used to investigate the effect of the geometry and morphology of porous solids on the transport of nano-confined fluids. It is demonstrated that the fully mutualized plug-like flow and fast transport which is commonly observed in slit pores do not present itself in rugose pores. Depending on the choice of pore model, transport diffusivity is observed to drop up to two orders of magnitudes; It is also observed that pore selectivity varies with rugosity level, which greatly alters the adsorption/transport of multi-component fluids. The different solid models used in this work are generalised using pore characteristic parameters. It is demonstrated that the transport coefficients are correlated to these parameters. This work has a direct impact on the understanding and modelling of unconventional hydrocarbon recovery and flow in organic shale rocks.

Keywords: Carbon nano-pores; Boundary-driven non-equilibrium molecular simulation; Adsorption; Carbon capture

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Chapter 1

Scope of work

1.1 Motivation and Objectives

Fluid transport in porous materials has long played a crucial role in industrial separation processes, where materials with specialized pores are designed to selectively permit the passage of specific molecules. A well-known example is seawater desalination, which employs reverse osmosis and has been studied since the 1960s.¹ Today, advances in controlling the shape and form of these materials are enhancing our understanding of confined fluid transport at the nanoscale. Popular porous structures, such as zeolites, silicas, and metal-organic frameworks (MOFs), have been designed and are extensively studied in both experimental and simulations settings.² These materials are lauded for their ability to facilitate the selective adsorption of specific molecules, making them indispensable in a variety of industrial applications.³ Additionally, porous carbons are gaining recognition for their suitability in efficient gas separations, hydrogen storage, and catalysis, owing to their chemical stability and cost-effectiveness.⁴ The ongoing research into optimizing the structure of these porous carbons is vital for enhancing their efficiency in these applications.

Moreover, understanding fluid transport in porous materials is crucial for

enhancing shale gas production, which is hindered by the inherently low permeability of kerogen.^{5,6} Various fracturing techniques are employed to enhance permeability, creating fissures that allow shale gas to exit the porous structure through diffusion.^{7,8} Furthermore, extremely thin yet strong porous membranes have been designed to be used in nanofiltration^{9,10} of shale oil. Therefore, understanding fluid transport in porous materials has direct merit in improving shale production.

This document aims to enrich today's comprehension of fluid transport in confined spaces, by developing robust techniques to evaluate fluid transport in nano-scaled pores, and addressing the existing knowledge gaps concerning the influence of surface rugosity on fluid transport. The following sub-sections provide a high-level overview of the main objectives of this work.

1.1.1 Developing methods for evaluating transport in porous materials

In many instances, given the nano-scale porosity of these materials, understanding the precise mechanism of mass transport is challenging. It is not known to what extent traditional kinetic and phenomenological models can be used to predict transport in these materials. Generally speaking, there are three theories used to characterize transport in porous materials. The first is based on Fick's law which employs an empirical constant to relate the transport (mass flux) to the macroscopic density (or pressure) gradient that drives the transport.¹¹ The strategy is conceptually straightforward and commonly implemented in the analysis of experimental results. However, the resulting coefficients suffer from many drawbacks, namely a lack of transferability, and a non-trivial pressure, temperature and concentration dependence. The Onsager formulation, based on irreversible thermodynamics,¹² recognizes that the driving force for transport is actually a gradient of chemical potential. The transport coefficients thus generated are fundamentally robust and better behaved than the Fickian counterparts, but are conceptually challenging as chemical potentials cannot be directly measured. A final formulation, defined as the generalised Maxwell-Stefan

theory,¹³ suggests the description in terms of so-called corrected diffusivities. There is a formal link between all these formulations.^{14,15} However, in all of these descriptions, there is a need to experimentally determine the transport coefficients, i.e. there are no currently available fully predictive methods.

Molecular dynamics (MD), Monte Carlo (MC), and a combination of both are commonly used in literature to study transport of pure fluids and multicomponent mixtures.^{16–18} Calculations can be based on the analysis of systems in or away from equilibrium.¹⁹ In equilibrium molecular dynamics (EqMD), the mean squared displacement, or velocities, of individual particles and their centres of mass are used to measure the motion of the fluid. To calculate transport diffusivities, additional information, namely adsorption isotherms, are included. Otherwise, the tracking of particle positions or velocities is employed to predict transport diffusivities of multicomponent mixtures.^{13,20–24} However, calculating transport diffusivities using equilibrium molecular dynamics requires very long simulation runs,²⁵ and additional simulations (typically Grand Canonical MC) to calculate Darken correction factors from adsorption isotherms ($\partial\mu/\partial \ln \rho$) are required. As an alternative, non-equilibrium molecular dynamics (NEMD) techniques have been developed measuring transport by inducing a flux by external fields or by artificial gradients.^{19,26}

The boundary driven NEMD (BD-NEMD) of Frentrop et al.²⁵ is a unique method of measuring transport diffusivities where MD is solely used to induce steady state density gradients across nanopores. This is done by applying an external field only to a small region in the simulation box, positioned far from the pore. This tool has been extensively used in literature for pure components,^{25,27–31} and mixtures.^{32,33}

Although BD-NEMD method has been used in literature, it is not known to what extent transport diffusivities measured with this procedure agree with other proven methods, such as EqMD. There are significant assumptions that need to be addressed to ensure that transport diffusivities measured from BD-NEMD and EqMD agree under all conditions. Moreover, although this method has been used to study multicomponent mixtures,³² only the self-transport coefficients have been measured,

and the effect of the cross-species transport coefficients have not been studied. The values of the cross-species transport coefficients have not been previously calculated using BD-NEMD, and it is not known to what extent transport diffusivities of multi-component mixtures measured using this method agree with those from EqMD simulation. This thesis aims to address these issues.

1.1.2 Investigating the effect of solid rugosity on transport

In literature, there have been many strategies in modelling the solid mesoporous materials to study fluid transport. The simplest representation of a mesopore is the slit pore, which is commonly used as a reference structure because of the well-known adsorption behaviour.^{34–38} As one of a multitude of examples, Kazemi and Takbiri-Borujeni^{39,40} studied flow of gases in perfect (2 and 5 nm) carbon slit pores. The understanding and qualification of the impact of defects on the flow of fluids through smooth ultraconfined pores, such as carbon nanotubes, has been recognised as a current knowledge gap in the field.⁴¹ It is clear that the concerted effect of wetting properties and surface roughness may considerably reduce friction of the fluid⁴² and in turn have a strong effect on transport, although the quantification of these effects is still an important research question. This is also relevant to shale extraction, where shale has complex micro and nanoporous characteristics with permeabilities which are orders of magnitude smaller than their conventional counterparts.^{43–46}

The correlation between the surface smoothness and fast plug flow was investigated by Castez et al.⁴⁷ by comparing ideal carbon nanotubes with nanotubes where the position of the carbons were randomised. It was found that disrupting the graphite structure and inducing atomic surface roughness would cause a significant drop in the transport of methane. This work was further extended⁴⁸ by adding tortuosity to the nanotube by twisting it. It was found that there was a slight drop in transport, much less significant than the effect of the atomic surface roughness. Phan and Striolo²⁸ studied the effect of adding blocks of solids inside slit pores to break the smooth flow of methane inside slit pores and found that hindrance to the flow by solid

blocks can significantly reduce transport of methane by up to five times. This was used to derive phenomenological correlations describing flow based on effective porosities and tortuosities. He et al.⁴⁹ studied the effect of large surface roughness on the flow of methane in slit pores, and it was shown that the velocity profiles of methane inside the rough pores are no longer plug like and that a parabolic velocity profile was observed for ridged and wavy surfaces.

Although the plug flow model of transport of oils in organic carbon pores has been used in large domain pore network models,⁵⁰ there are key questions that have not yet been addressed. Firstly, transport selectivity of hydrocarbon mixtures have not been studied for liquid mixtures. Secondly, as suggested by previous studies for gases,^{47,49} surface roughness affects transport of gases in organic pores, however, the effect of surface roughness on the flow of hydrocarbon liquids has not been systematically studied. This is important given that realistic kerogen pores are not perfect slit pores and, presumably, the roughness can significantly affect transport. Finally, although velocity profiles are usually the parameters studied in mesoporous materials, it is important to understand transport in the context of transport coefficients and/or permeabilities. It is known that permeability of fluids in shales is in the order of nanodarcy (nD),⁵¹ however, whether slit (or rugose) pore models can have permeabilities in the same order of magnitude is yet to be determined.

1.1.3 Characterisation of rugose carbon models

A large amount of research has been dedicated to studying carbon-based solids as they are highly relevant in gas separation and ubiquitous in organic matrix-related work.⁵² Common representations of carbon pores include carbon slit pores and carbon nanotubes (CNTs), both of which have ideal smooth surfaces.^{39,40,53–58} In these cages, the characterization of the pore geometry is trivial, as the pore height (or pore diameter) fully describes the geometry. Both surface rugosity and tortuous pore morphology complicate the description of the pores and affects the observed transport. Some relevant work has been carried out to resolve this matter: He et al.⁴⁹ studied the

effect of large-scale roughness on methane transport in graphite pores and noted the disruptions of the parabola velocity profile. Additionally, Phan and Striolo²⁸ added solids blocks inside slit pores to generate a collection of pores with various characteristic parameters. Their results demonstrated a linear relationship between methane transport and a pore characteristic parameter. It is, however, unclear to what extent these conclusions can be extended to other scenarios.

1.1.4 Understanding the effects on CH₄/CO₂ mixtures

Currently, there are few studies focusing on multicomponent mixtures and how surface roughness affects their transport behaviour.^{59,60} Zhu et al.⁶¹ studied the transport diffusion mechanism of CH₄/CO₂ mixtures in shale nanopores. They observed that CO₂ injection weakens the CH₄ surface diffusion and reported the critical rule of pore size in determining the transport mechanism. Sun et al.⁶² investigated the competitive adsorption of CH₄/CO₂ mixtures in shale matrix. They reported significant effect of pressure and rugosity on competitive adsorption. The challenges inherent in these studies can be categorized into two main aspects: firstly, the absence of metrics to define pore characteristics that impact transport, and secondly, the need for effective tools to calculate transport properties. This thesis seeks to address and overcome these challenges.

1.2 Thesis Overview

Chapter 2: The study of fluid transport, particularly diffusion, has been a continuous theme in research throughout history. Its significance extends across numerous disciplines and is of paramount importance. This chapter provides a summary of the breakthroughs and advancements in this field, underscoring some of the most pivotal models and experiments.

Chapter 3: The focus shifts to the application and theory behind computer simulation techniques. This chapter offers a comprehensive discussion of the

Boundary-Driven Non-Equilibrium Molecular Dynamics methodologies that is central to this project, providing detailed descriptions of its implementation and relevance to the study.

Chapter 4: The Boundary-Driven Non-Equilibrium Molecular Dynamics for evaluating mass transport coefficients of fluids in nanoconfined media is revisited and extended to multicomponent mixtures. The study provides examples of calculating diffusion coefficients for various systems. The results show that this method is robust and well-suited for studying liquid flow in nanoconfined media.

Chapter 5: This chapter presents the results of modeling the transport of n-octane and n-hexadecane, both individually and as mixtures, through carbonaceous nanopores under high-pressure conditions. The pores are represented as smooth slit sheets with added perturbations in the form of ridges and steps. One key finding of this work is that smooth slit carbon pore models, often used as surrogates for kerogen regions in shale, do not adequately represent ultra-confined natural pores. The study also highlights the presence of important cross-correlation effects, which influence the way components of the mixture flow together.

Chapter 6: This chapter reports molecular simulations of the adsorption and transport behaviour of CH_4/CO_2 mixtures in two types of non-ideal carbon nanopores. One model decorates an otherwise slit pore with surface imperfection which disrupts the smooth walls; a second model considers a disordered media with significant tortuosity. The study suggests that the performance of CO_2 -enhanced oil recovery may be overestimated by the smooth pore models. In addition, a pore characteristic factor is seen to be appropriate to correlate the transport diffusivities in nano-pores.

Chapter 7: This chapter provides an overview of the accomplishment in this work and discuss the implications of the results. This information provides a guideline to the direction of future research.

Chapter 2

Fluid Diffusion - Models and Experiments

2.1 From continuum to explicit models

Fluid transport is a diverse field of study that explores the movement of liquids and gases within specific environments. This subject has captivated the attention of researchers across various disciplines due to its wide-ranging applications. One particularly aspect of this study is fluid diffusion, which has garnered significant interest for its implications in crucial areas such as membrane separations and the recovery of crude oil resources.⁶³ The attempt to unravel the obscurity of the diffusive mechanism can be traced back to 18th century. In 1748, Jean-Antoine Nollet made a groundbreaking discovery in the field of fluid diffusion. He was the first to link permeation with differences in concentration, a phenomenon now known as osmosis.⁶⁴ Nollet's discovery sparked a surge in research on fluid diffusion, among those, the most salient work was done by Thomas Graham and Adolf Fick. Graham took an interest in gas diffusion and delved deep in pure gas diffusion.⁶⁵ He devised experiments to measure changes in gas concentration as a means to determine diffusion rates. Through these experiments, Graham compiled data on the diffusion of seven different gases and established that diffusivity is inversely proportional to the

square root of gas density.⁶⁶ Conversely, Fick's work focused on diffusion in liquid. In his experiments, he employed two separate reservoirs filled with saltwater of varying concentrations. By observing the changes in salt concentration over time, Fick calculated diffusivity. His work culminated in the publication of Fick's law in 1855, a fundamental principle stating that diffusive flux is directly proportional to differences in concentration.⁶⁷ Fick's contributions form the foundation of contemporary understanding of fluid diffusion, serving as the basis for numerous modern models and theories that remain influential to this day.⁶⁸

During Fick's period, the prevailing scientific consensus considered matter as a continuous bulk, and researchers constructed models based on this conventional perspective. This was primarily because the concept of atoms was not widely accepted at the time, which limited the sophistication of their approaches by today's standards.⁶⁹ In 1827, Robert Brown published his work on Brownian motion which initiated the transition from the continuum approach to the atomistic approach.⁷⁰ In his experiment, a seed was submerged in water and observed under a microscope. It was noted that the observed random motion "arose neither from currents in the fluid nor from gradual evaporation".⁷¹ This discovery sparked debates about the fundamental nature of matter, which persisted until 1905 when the renowned theoretical physicist Albert Einstein introduced a mathematical model. This model attributed the random motion of the seed to its frequent collisions with water molecules, and put an end to the debate.^{72,73} During this period, researchers who favoured the atomistic approach developed new models for fluid transport based on molecular interactions. James Maxwell believed that one can construct the macroscopic property of a bulk fluid by understanding the microscopic property of individual particle inside the system. Based on this concept, Maxwell, along with Josef Stefan, formulated the Maxwell-Stefan model. This model postulates that the frictional forces acting between fluid particles balance the diffusive driving forces, which is typically characterized by chemical potential gradients. Atomistic descriptions such as Knudsen models and dust-gas models followed. This shift in perspective not only enhanced the comprehension of

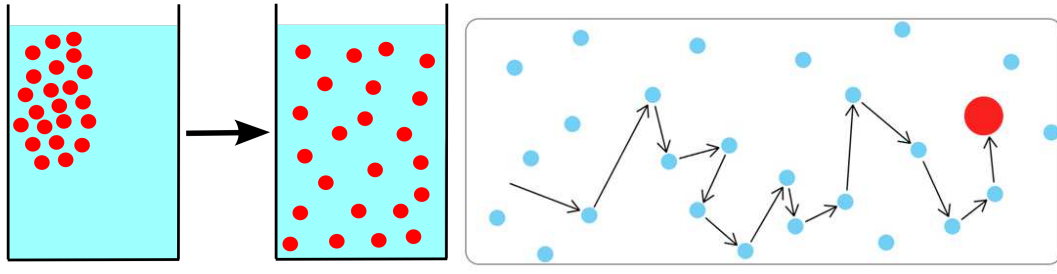


Figure 2.1: Illustrations of diffusion process (left) and Brownian motion (right). The large red dot represents the suspended particle.⁷⁴

bulk fluids but also facilitated the examination of fluid transport in confined spaces, particularly at the atomic scale. In this review, we will take a step back and highlight a few of the most significant models designed for these specific purposes.

2.2 Diffusion models for bulk fluids

2.2.1 Fickian model

The Fickian model links the diffusive flux to the concentration gradient of the fluid. In simpler terms, it implies that fluid tends to move from regions of high concentration to those of lower concentration until concentration is uniformly distributed. This model is fundamental for understanding the process of diffusion in various systems. The transport diffusivity (Fick diffusivity) of a single component fluid is

$$J = -D\nabla\rho \quad (2.1)$$

Where J is the flux of the fluid, D is the transport diffusivity, and $\nabla\rho$ represents the fluid concentration gradient. In many cases, transport in one particular direction (for example, x) bears more interest and equation (2.1) can be written as

$$J_x = -D\frac{\partial\rho}{\partial x} \quad (2.2)$$

The Fickian model has been widely adopted due to its straightforward formulation.

Its simplicity is a key advantage because both concentration differences and diffusive flux can be easily measured in experiments. This ease of use has led to its widespread use in engineering and scientific research. However, the model's simplicity also comes with a drawback. Krishna pointed out a limitation of the Fickian model, specifically its failure to account for the influence of external disturbances.⁷⁵ This issue was demonstrated in experiments conducted by Duncan and Toor in 1962,⁷⁶ where a system of ternary gas diffusion was studied. In their research, nitrogen was carried by the diffusive flow of hydrogen and oxygen. Therefore, despite there being no concentration difference for nitrogen, it exhibited a net flow. This finding revealed that the cross-term interactions between different gas species had a profound effect on the transport of individual components, an aspect that the Fickian model does not consider. In addition, Vinograd and McBain⁷⁷'s diffusion experiments with charged electrolytes mixtures show Fickian model fails to incorporate electromagnetic interactions. Kapteijn et al. experimented with long-chain hydrocarbon mixtures and shows that molecule size has a profound effect on diffusion.⁷⁸ There are other instances where the limitations of the Fickian model become apparent, such as when modeling transport at a vapor-liquid interface where a density gradient across the interface does not induce a flow. These examples underscore the need for modeling transport at an atomistic level, where the interactions between individual molecules can be considered.

Despite this, Fick's model still holds its utility, particularly in scenarios involving dilute fluid mixtures where molecular interactions are minimal. In such cases, the simplicity and practicality of the Fickian model make it a valuable tool for estimating diffusion and concentration changes.

2.2.2 Maxwell-Stefan model

The Maxwell-Stefan model^{23, 79, 80} is an atomistic approach used to calculate diffusivity by accounting for the mechanical forces acting on individual particles. Consider a binary mixture within a control volume where the two fluid species have average velocities of

u_1 and u_2 . When the system is at a steady state, the flow inducing force is at equilibrium with the frictional force.

The Maxwell-Stefan model attributes the source of the driving force to the gradient of the chemical potential, represented as $\nabla\mu$, and it takes into account the drag force as the friction between the two fluid components. This model offers a more detailed and comprehensive description of diffusion in binary mixtures compared to the Fickian model by considering the interactions and movements of individual particles. Therefore, a force balance on species 1 is:

$$-\nabla\mu_1 = \frac{k_B T}{D_{12}^{MS}} x_2 (u_1 - u_2) \quad (2.3)$$

where D_{12}^{MS} is Maxwell-Stefan diffusivity, $(u_1 - u_2)$ is the difference in average velocity, x denotes the molar composition, and $k_B T / D_{12}^{MS}$ can be interpreted as drag coefficient. Multiplying both side of equation (2.3) by $x_1 / k_B T$ relates fluid flux J_1 to Maxwell-Stefan diffusivity D_{12}^{MS} and chemical potential gradient $\nabla\mu_1$.¹³

$$-\frac{x_1}{k_B T} \nabla\mu_1 = \frac{x_2 J_1 - x_1 J_2}{c_t D_{12}^{MS}} \quad (2.4)$$

Where c_t is the total concentration of fluids. This equation can be extended to multi-components mixture, where the chemical potential driving force on one species is in balance with the total friction force with every other species.¹³

$$-\frac{x_i}{k_B T} \nabla\mu_i = \sum_{j=1, j \neq i}^n \frac{x_j J_i - x_i J_j}{c_t D_{ij}}, j = 1, 2, 3, 4, \dots \quad (2.5)$$

2.3 Transport models for confined fluids

To study fluid transport in porous media, it is paramount to recognise the dominant forces that govern the adsorption performance within the pore. The unique combination of pore size and fluid density leads to fluid transport operating in distinct

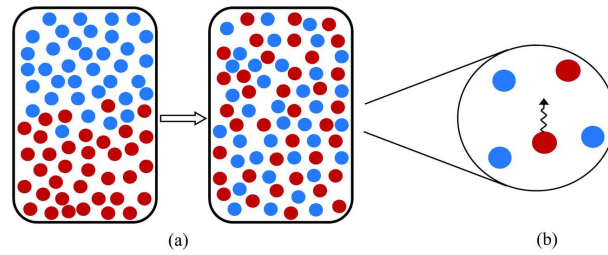


Figure 2.2: (a) The mutual diffusion coefficient is related to the collective motion of all the components due to a chemical potential gradient. (b) The self-diffusion coefficient is related to the motion of the individual components in a mixture at equilibrium.⁸¹

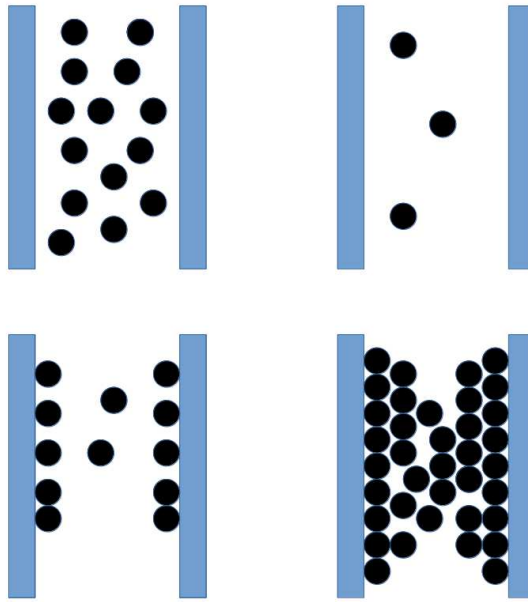


Figure 2.3: Transport mechanisms in porous media: molecular or gaseous flow (top left), Knudsen flow (top right), surface diffusion (bottom left), capillary condensation (bottom right)

diffusive regimes. Here we discuss four well known diffusive mechanisms, each of which plays a significant role in the study of fluid transport in porous materials (Fig 2.3).⁸²

Gaseous diffusion is strongly associated with the classic modelling techniques when the strategy is based on the continuum bulk approach.⁸³ It occurs when the pore diameter is larger than the mean free path of the fluid molecule, and the collisions between molecules are more frequent than those between molecules and the pore surfaces. Due to the infrequent interaction between fluid and solid, Fick's law is often

adequate in describing this diffusive scheme.⁸⁴

Conversely, Knudsen diffusion is on the side of the spectrum compared to gaseous diffusion. It is a diffusion mechanism that occurs when the scale length of a system is comparable to or smaller than the mean free path of the particles involved.⁸⁵ This phenomenon is more pronounced when molecules move through narrow pores with diameters between 2 and 50 nanometers (mesopores), as they frequently collide with the pore walls. In cases where the pore diameter is smaller than the mean free path of the diffusing gas molecules and the gas density is low, the gas molecules collide with the pore walls more frequently than with each other, resulting in Knudsen diffusion.⁸⁶

Surface diffusion occurs when diffusing molecules have a preference for adsorbing onto the pore surfaces.² In this regime, a dense mobile adsorption layer can form, which significantly increasing the flow of molecules along the surface. An extension of this regime is known as multiplayer diffusion, which is associated with higher adsorption density, leading to even more complex dynamics involving multiple layers of adsorbed molecules diffusing on the surfaces.⁸⁷

Capillary condensation occurs when the adsorbed density is further increased beyond the multilayer diffusive regime. In this regime, the diffusing component condenses inside the pore, and then evaporates at the other end of the pore. This behavior is a result of the interactions between the confined fluid and the pore walls, and it plays a significant role in the behavior of fluids in porous materials.⁸⁸

2.3.1 Hagen-Poiseuille model

The most straightforward methods to describe flow in porous materials are based on classic fluid mechanics. In those models, continuum hydrodynamic flux is driven by a pressure difference in a simple geometry. The momentum of the flux is described using the Navier-Stokes equation, allowing for the estimation of transport properties. An example of such a model is the Hagen-Poiseuille model, which is particularly useful for describing the flow of incompressible Newtonian fluids within smooth cylindrical pores. This model is fundamental for understanding fluid flow in such geometries and

has various practical applications.⁸⁹ By assuming non-slip condition at the solid-fluid interface, the Hagen-Poiseuille equation is given as

$$\Delta P = -\frac{8\mu LQ}{\pi r^4} = -\frac{8\pi\mu LQ}{A^2} \quad (2.6)$$

Where ΔP is the pressure drop across the pore, Q is the fluid volumetric flow rate, L is the length of the pore, r is pore radius, μ is the fluid dynamic viscosity and A is the cross-section of the pore. By using $J = \rho u$, one can rearrange the equation (2.6) into

$$\frac{dp}{dx} = -\frac{32\eta u}{d^2} \Rightarrow J_x = -\frac{d^2}{32\eta} \frac{dp}{dx} \quad (2.7)$$

Where p represents pressure, d donates the pore diameter and η is the kinetic viscosity of the fluid. Note that the equation form is analogous to the assessment of permanence,⁹⁰ which is a phenomenological observation that the permeating flux through a porous solid is proportional to the pressure difference across the material.

$$J_x = -K \frac{dp}{dx} \quad (2.8)$$

Both expressions associate the flow with a pressure gradient, and the term K reflects permeance.

The validity of non-slip conditions in narrow confinements has been a subject of frequent debate and questioning. Numerous studies have presented counterexamples where the flow at the interface exhibits a substantial contribution to the overall flux. For instance, Hummer and Majumder observed high flux in carbon nanotubes and attributed this enhanced flow to the concept of slip length.⁹¹ Schematically, the slip length can be obtained by extending the velocity profile and measuring the length from the wall to the non-slip point. Mathematically, it is estimated using the ratio of the wall velocity to the velocity gradient.⁹² The incorporation of slip length into the fluid dynamics equations results in an increased estimation of flux, leading to a modified equation to account for slip effects.

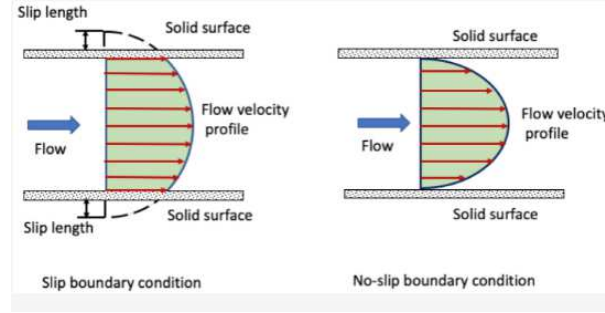


Figure 2.4: Illustration of the Hagen-Poiseuille and Slip flow model⁹³

$$J_x = -\frac{(d^2 + 8dL_s)}{32\eta} \frac{dp}{dx} \quad (2.9)$$

where L_s is the slip length and it is defined as

$$L_s = \frac{u_{wall}}{du/dr} \quad (2.10)$$

Although the Hagen-Poiseuille model is useful for describing macroscopic systems, it is necessary to scrutinize confined transport at the molecular scale. Due to the influence of discrete molecular collisions and variations in local density and viscosity, incorporating molecular interactions become crucial for modelling.

2.3.2 Knudsen model

The Knudsen diffusion model is a widely accepted approach for describing low-density gas behavior in cylindrical pores. This model assumes that the momentum transfer rate between the fluid and the pore wall exceeds that between the diffusing gas molecules. This criterion can be assessed by comparing the mean free path of gas molecules, represented as λ , with the size of the pore, denoted as L . The ratio λ/L yields a dimensionless parameter known as the Knudsen number, typically denoted as K_n . The Knudsen number serves as an indicator to determine the appropriateness of the Knudsen diffusion model for a specific system.

$$K_n = \frac{\lambda}{L} \quad (2.11)$$

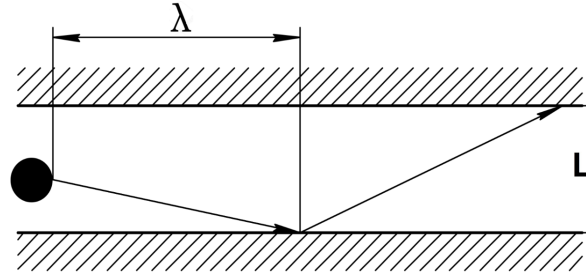


Figure 2.5: Illustration of Knudsen diffusion model in a slit pore. The mean free path of the gas molecules is denoted as λ . Whereas the pore size is denoted as L .

The mean free path of an ideal fluid at a gaseous state can be calculated from its temperature and pressure via the equation(2.12)⁹⁴

$$\lambda = \frac{k_B T}{\sqrt{2} \sigma_c^2 P} = \frac{1}{\sqrt{2} \sigma_c^2 c} \quad (2.12)$$

Where σ_c is the collision diameter, k_B is the Boltzmann constant, and c is the fluid concentration.

When K_n is greater than 1, the criterion for the Knudsen model is met and the Knudsen diffusivity D_{kn} is⁸⁵

$$D_{kn} = \frac{L}{3} \sqrt{\frac{8k_B T}{\pi m}} \quad (2.13)$$

Where L is the pore diameter, m denotes the molecular mass, T is the temperature and k_B is the Boltzmann constant.

Despite its success in describing confined diffusion of diluted gas, the Knudsen model has limitations. Firstly, the model assumes diffusive reflection during momentum exchange, which may not accurately represent the behavior of gas molecules when they encounter a rugose wall.⁸⁵ In addition, Knudsen's model does not incorporate the effect of adsorption, which has a profound impact on fluid transport in nanopores. As the complexity of solid structures and solid-fluid interactions increases, relying on a single criterion to determine the nature of fluid flow becomes insufficient.⁸⁶

2.3.3 Dusty gas model

The dusty-gas model, developed based on kinetic theory, derives from the Maxwell-Stefan diffusion model. In this model, solids are treated as a collection of uniformly distributed inert particles.^{95,96} This introduces the concept of friction between the fluid and these solid "dust" particles, which needs to be taken into account in the force balance equations. To achieve this, one can use the generalized Maxwell-Stefan equation and consider the solid wall as an additional "n+1" species.⁷⁵ This model provides a framework for understanding the behavior of gas mixtures in the presence of solid particles, which can be applicable in various engineering and scientific contexts. Under the ideal gas assumption and based on the general form of the Maxwell-Stefan diffusion equation, the dusty gas model can be written as Eq. 2.14 for a binary fluid. w represents wall particles and $u_w = 0$

$$-\nabla\mu_1 = \frac{k_B T}{D_{12}^{MS}} x_2 (u_1 - u_2) + \frac{k_B T}{D_{1w}^{MS}} u_1 \quad (2.14a)$$

$$-\nabla\mu_2 = \frac{k_B T}{D_{21}^{MS}} x_1 (u_2 - u_1) + \frac{k_B T}{D_{2w}^{MS}} u_2 \quad (2.14b)$$

The dusty gas model is extensively used in modelling gas diffusion in confinement, such as the transport of organic vapour in soil.⁹⁷ However, a major drawback lies in the assumption of a uniform distribution of dust particles, which may not accurately reflect real-world scenarios. Additionally, the model relies on constant values for confined fluid density and viscosity, which deviate from reality. Within a pore, these properties can exhibit significant variations due to intricate interactions among the fluid, solid structure, and temperature fluctuations. Consequently, the dusty gas model tends to be inadequate when confronted with non-ideal conditions and dense fluids. In situations where the actual system diverges substantially from these assumptions, more advanced models and techniques become essential for providing precise predictions and descriptions of gas diffusion in confined spaces.

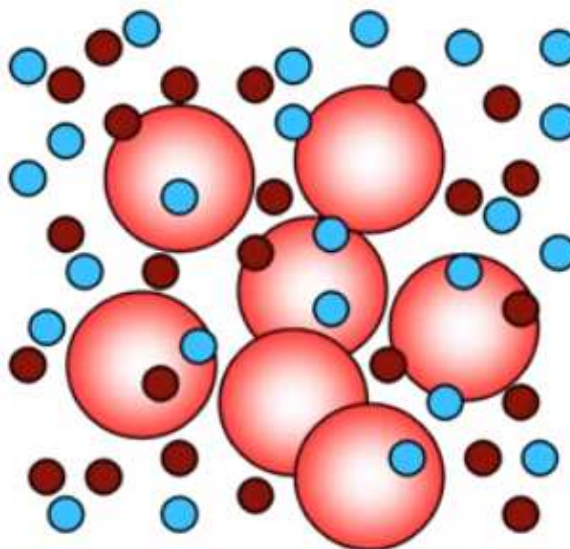


Figure 2.6: Illustration of dusty gas model for a binary system, the large red sphere represents the stationary wall particles, while the blue and purple spheres represent the fluid particles.⁹⁸

2.4 Porous carbon modelling

Porous carbon materials have a wide range of applications, from gas storage and separation to energy storage and catalysis. To study their characteristic and understand their implication on fluid transport, it is crucial to develop accurate models that describe the complex structures and behaviors of these materials.⁹⁹ In this section, we explore various models used to represent porous carbons, ranging from simple representations like slit pore models to more sophisticated approaches like the Segarra and Glandt model.¹⁰⁰ These models serve as valuable tools in studying the properties and behavior of porous carbons, offering insights into their atomic and structural arrangements, porosity, and adsorption characteristics. Understanding these models is essential for tailoring porous carbon materials for specific applications and improving their performance in various industrial and scientific fields.

2.4.1 Slit pore models

In the pioneering work by Seaton et al.¹⁰¹, a molecular model was introduced to characterize the pore size distribution of activated carbons. In this model, carbon pores were represented as slits positioned between infinitely extended graphitic walls. The simplicity and effectiveness of this slit pore model have since made it the standard approach in the development of methods for characterizing various carbon materials. The solid–fluid interaction potential in this model was described by the closed form formula of Steele et al.¹⁰²

In order to clearly describe a slit pore model, it is important to address the issue of how one defines the pore height. The definition of the pore height in this thesis can be best understood using Figure 2.7. First, a packed solid structure is generated, fully periodic in all dimensions. Then, the y dimension of the simulation box is increased by a distance equal to the pore height. The pore height, H , corresponds to the distance between the planes defined by the outer most points of the exposed surface beads defined by their characteristic diameter. Clearly, other definitions of H may be used.^{103,104} However those alternative definitions will not have influence on the main conclusions of this thesis.

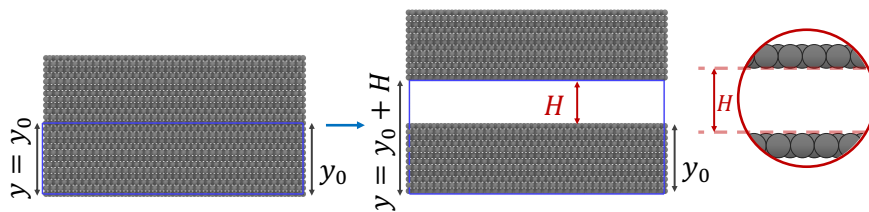


Figure 2.7: Pore height is systematically defined by having a fully periodic solid with no accessible pore height, and then increasing the y dimension of the simulation box by the value of the pore height, H .

The carbon slit pores in this document are modelled as stacked graphite sheets: atoms in a graphene sheet bond with the three nearest neighbours 120 degrees apart to form a hexagonal lattice which is then stacked together to build a graphite structure. The distance between neighbouring carbon atom is 1.4 Å and the distance between neighbouring graphene sheets is 3.4 Å.

Although slit pores are a popular choice in the literature, they have notable drawbacks. The assumption of smooth surfaces has been reported to significantly near-surface transport.¹⁰⁵ The non-uniformity of the adsorption field near the edges also alters the characteristics of adsorption, a phenomenon known as the "edge effect." This effect is most pronounced in systems where the pore length is comparable to its width.¹⁰⁶ Therefore, more sophisticated models are required to address these limitations.

2.4.2 Branched-tree model

This advanced model highlights the diverse range of porosity sizes present within porous carbon, spanning from micro to macro porosity. It suggests the potential for material transport across pores ranging from the widest to the narrowest.¹⁰⁷

Regrettably, the model has limitations as it assumes a direct progression from microporosity to mesoporosity. This depiction can foster misconceptions about the actual structure of the carbon network, as it may not accurately reflect the intricate relationships between different porosity levels.

2.4.3 Segarra and Glandt model

The Segarra and Glandt¹⁰⁰ model represents activated carbon as an isotropic assembly of three-dimensional circular platelets, each composed of two graphitic planes. This model generates the structure of the adsorbent as a three-dimensional arrangement of hard platelets in thermodynamic equilibrium using canonical Monte Carlo simulation. It captures some of the heterogeneous features of microporous carbon, including edge effects, pore connectivity, and various pore shapes. However, it does not account for the atomic structure of graphene planes in real carbons or other factors such as platelet size. Despite these limitations, it offers a more realistic representation than the slit pore approach without the complexity of fully atomistic models.



Figure 2.8: The branched tree model illustrating the connected porosity.¹⁰⁸

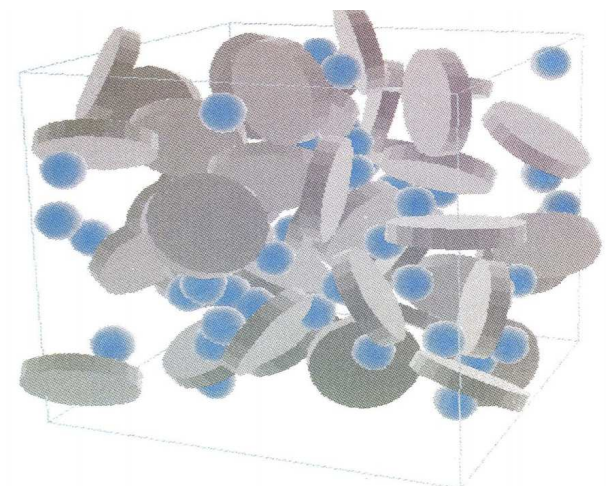


Figure 2.9: An assembly of graphitic platelet model contains a distribution of different carbon surfaces using the Segarra and Glandt¹⁰⁰ model.

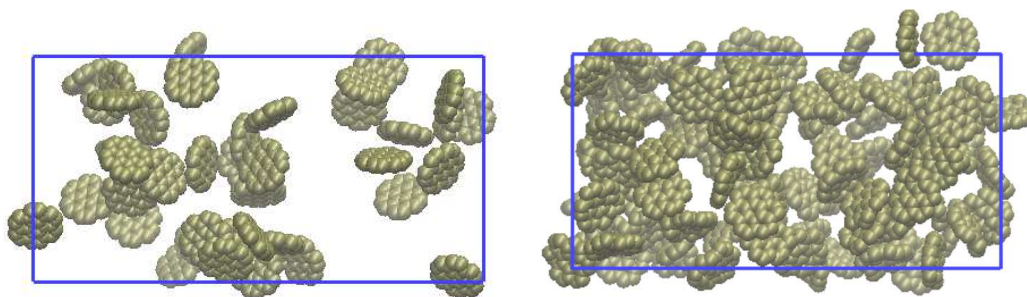


Figure 2.10: Snapshots of coronene fragments model. Number of fragments equals 40 (left) and 120 (right)

2.4.4 Coronene Fragment model

The coronene fragments model is a collection of suspended coronene-shaped carbon fragments that functions as a porous matrix. This carbonaceous model inherits its basic structure from a model by Segarra and Glandt¹⁰⁰ where disk-like carbon platelets are randomly placed in a simulation cell to take into account the balance between the non-uniform porosity of carbons and the inherent layering of sp^2 carbons. This model was initially proposed by Salih¹⁰⁹ and has been extended by Kumar et al.^{110,111} using small coronene building units. To set up this structure, simulation boxes were filled with different densities of coronene fragments. The fragments undergo random thermal motion and their instantaneous configuration at the end of the simulation is recorded.

2.4.5 Hybrid Reverse Monte Carlo models

Jain et al.^{112,113} present a method to generate porous carbon structures using the Hybrid reverse Monte Carlo Method. In their research, the acceptance probability for atomic movements incorporates an energy term, with the aim to reduce the total energy of the system and minimize errors in the radial distribution function. The inclusion of the energy term significantly reduces the occurrence of impractical, high-energy structures in the generated models, while also aligning well with experimental data.

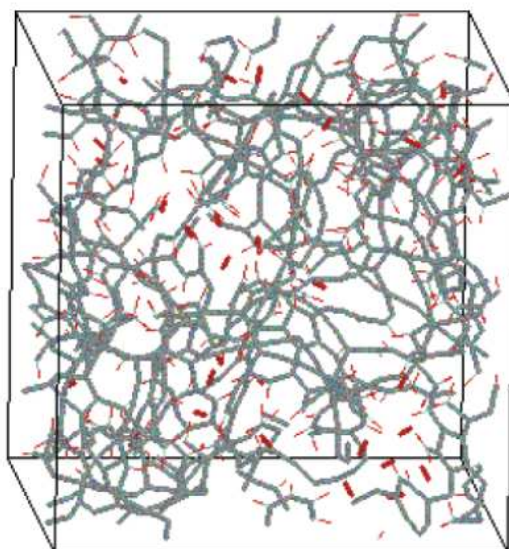


Figure 2.11: Snapshots of models of saccharose cokes obtained from the HRMC method. The gray rods represent C-C bonds, and the red rods represent C-H or H-H bonds.¹¹²

Chapter 3

Molecular simulation - Theory and Methodology

3.1 Computer simulation

Beyond laboratory work and modelling, the utilization of computer simulation methods has revolutionized our ability to investigate and comprehend fluid transport in porous media. This powerful approach has provided researchers with a virtual laboratory to explore the intricate dynamics of fluid flow within the complex porous structures. Here we aim to provide an overview of the fundamental theories and methodologies that have been developed in this field.

3.1.1 Statistical Mechanics

In essence, statistical mechanics is the link between the macroscopic properties and microscopic interactions. It aims to describe the statistical behaviour of these particles and how their collective interactions result in observable physical phenomena.¹¹⁴ This section will give a brief overview of this topic as a prerequisite knowledge for this work.

In classic thermodynamics, system states are defined by a set of parameters, for

example, the number of particles N , the temperature T and the pressure P . Other thermodynamic properties such as entropy, chemical potential can be calculated from the known ones through an equation of state (EoS). On the other hand, systems can be described by the position q and momenta p of all particles in the system. This is called a microstate, which is associated with a Hamiltonian energy $\mathcal{H}$. The momenta configuration p of a microstate contributes to the kinetic energy $\mathcal{K}(p)$, and the momenta q contributes to potential energy $\mathcal{V}(p)$, the sum of those two energy is the Hamiltonian.¹¹⁵

$$\mathcal{H}(p, q) = \mathcal{K}(p) + \mathcal{V}(q) \quad (3.1)$$

Statistical mechanics posits that macroscopic properties are derived from time averages over a vast number of microscopic states. For instance, temperature is defined as the average kinetic energy of the system. This theory is built on the assumption that systems can be taken to the thermodynamic limit, where the number of particles N in the system approaches the Avogadro number. At this scale, the differences in observable thermodynamic variables among different microstates are considered negligible. In a state of equilibrium, a particle characterized by its position and momentum occupies a phase space with a probability distribution that remains independent of time. An essential concept to introduce here is ergodicity, which suggests that a sufficiently large collection of random samples from a process can represent the average statistical properties of the entire process. Rather than focusing on a single system evolving through a phase space of positions and momenta, statistical mechanics considers an infinite number of such systems, each subject to macroscopic thermodynamic constraints. Each microstate satisfying these constraints is called an ensemble, and the type of ensemble is determined by the specific thermodynamic constraints in place:¹¹⁶

1. Canonical NVT ensemble, constant number of particle N , constant volume V , constant temperature T .
2. Isobaric/Isothermal NPT ensemble, constant number of particle N , constant

pressure P , constant temperature T .

3. Grand canonical μVT ensemble, constant chemical potential μ , constant volume V , constant temperature T .

4. Micro canonical NVE ensemble, constant number of particle N , constant volume V , constant total energy E .

The probability of a given microstate with energy E_i in the canonical NVT ensemble follows a Boltzmann distribution:

$$P(E_i) = \frac{\exp(-\beta E_i)}{\sum_{i=1}^N \exp(-\beta E_i)} \quad (3.2)$$

Where $\beta = 1/(k_B T)$ and k_B is the Boltzmann constant. The denominator is called the canonical partition function Q , which is a normalisation factor that represents all possible states of such distribution. It will be shown that this function is the key to converting microscopic configuration to classical thermodynamics variables.

$$Q = \sum_{i=1}^N \exp(-\beta E_i) \quad (3.3)$$

Since the probability of a particular microstate is known, one can calculate the ensemble average energy $\langle E \rangle$ as

$$\langle E \rangle = \frac{\sum_{i=1}^N E_i \exp(-\beta E_i)}{\sum_{i=1}^N \exp(-\beta E_i)} = \frac{\sum_{i=1}^N E_i \exp(-\beta E_i)}{Q} \quad (3.4)$$

Notice that

$$\sum_{i=1}^N E_i \exp(-\beta E_i) = -\frac{\partial Q}{\partial \beta} \quad (3.5)$$

$$\langle E \rangle = -\frac{1}{Q} \frac{\partial Q}{\partial \beta} = -\frac{\partial \ln Q}{\partial \beta} \quad (3.6)$$

It is clear that the partition function Q is all that is required to calculate the average energy. For simple system, this average energy equal to the internal energy U , which can be transformed into Helmholtz free energy to provide physical interpretation of the system:

From the Gibbs fundamental relation,

$$A = U - TS \quad (3.7)$$

Where S is the entropy, divide both side by T ,

$$\frac{A}{T} = \frac{U}{T} - S \quad (3.8)$$

By differentiating with respect to T :

$$\frac{\partial}{\partial T} \frac{A}{T} = \frac{\partial}{\partial T} \left(\frac{U}{T} - S \right) = -\frac{U}{T^2} = \frac{1}{T^2} \frac{\partial \ln Q}{\partial \beta} = -k_B \frac{\partial \ln Q}{\partial T} \quad (3.9)$$

Integrating both side by T yields the key bridging equation from Q to A . Other macroscopic properties can be determined from the classic thermodynamics relations.

$$A = -k_B T \ln Q \quad (3.10)$$

Thus far the link between microscopic configuration and macroscopic properties has been addressed. To assess Q , recall that Hamiltonian is a function of the position and momenta of all particles. Because those two variables are independent, we arrive at a different way to express the partition function.

$$Q = \frac{1}{h^{3N} N!} \int \exp(-\beta \mathcal{K}(p^N)) dp^N \int \exp(-\beta \mathcal{V}(q^N)) dq^N \quad (3.11)$$

where q^N is the position of N -th particles and p^N is the momenta. The factor $h^{3N} N!$ is added to account for the phase-space volume of each quantum state and the indistinguishability of particles. One can rewrite the equation above as $Q = Q_{ideal} Z$, where Q_{ideal} is the partition function due to momenta only, which has an explicit mathematical form.

$$Q_{ideal} = \frac{1}{h^{3N} N!} \int \exp(-\beta \mathcal{K}(p^N)) dp^N \quad (3.12)$$

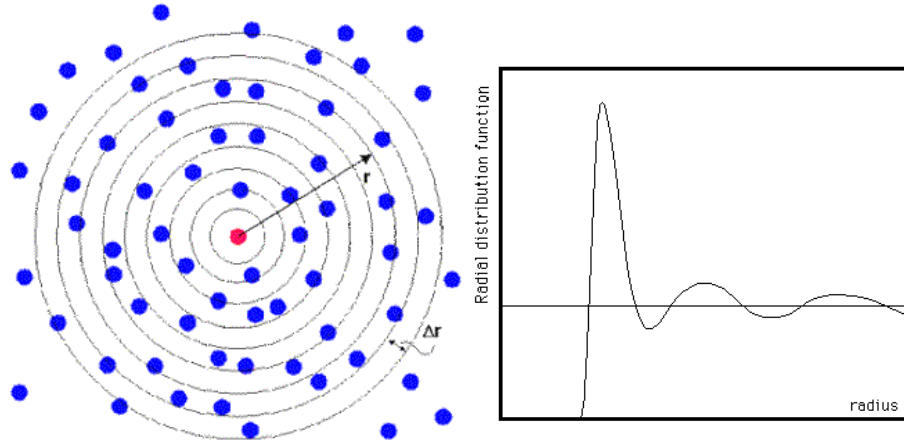


Figure 3.1: An example illustration of radial distribution function $g(r)$.¹¹⁸

$$Z = \int \exp(-\beta \mathcal{V}(q^N)) dq^N \quad (3.13)$$

Z is the partition function that is contributed by the interaction in the system. Considering the scale of N , it is impossible to carry out the exact integration to evaluate Z . However, it is possible to reduce the dimensionality of the problem by only considering pair potentials. Normally, the full interaction energy is defined by adding the potential energy of individual particles due to the external field, followed by the summation of all pairwise intermolecular interactions, followed by the triplet contribution and so on. In practice, it is common to truncate the 3rd, 4th and higher-body interactions for a large system.

$$\langle \mathcal{V}(q^N) \rangle = 2\pi\rho N \int_0^\infty g(r)u(r)r^2 dr \quad (3.14)$$

where $g(r)$ is the radial distribution function, $u(r)$ is the pair wise interaction. Therefore, it is critical to have an accurate description of $u(r)$.¹¹⁷

3.1.2 Molecular interactions

While statistical mechanics offers a framework for deducing thermodynamic properties from microscopic configurations, it's crucial to have a precise model of pairwise potentials $u(r)$ to make this approach effective. These intermolecular models

can be derived from quantum mechanics, providing a fundamental understanding of the forces at play, or they can be developed by fitting thermodynamic properties obtained from experimental measurements. The accuracy and reliability of these pairwise potential models are critical in ensuring meaningful and accurate predictions for a wide range of physical and chemical phenomena.

From a classical Newtonian description, the force F between two particles given an interaction potential $u(r)$ is:

$$F = -\frac{du(r)}{dr} \quad (3.15)$$

Some most widely-used potential model includes hard-sphere model,¹¹⁹ square-well potential¹²⁰ and Mie model.¹²¹

Mie potentials

Mie presented a groundbreaking article in 1903 that delved into intermolecular potentials.¹²¹ In this work, Mie derived a vapor pressure equation and an EoS specifically tailored for monatomic fluids. Employing modern nomenclature, the Mie potential can be written as.¹²²

$$u^{Mie}(r) = C\epsilon \left[\left(\frac{\sigma}{r} \right)^{\lambda_r} - \left(\frac{\sigma}{r} \right)^{\lambda_a} \right] \quad (3.16)$$

Where

$$C = \left(\frac{\lambda_r}{\lambda_r - \lambda_a} \right) \left(\frac{\lambda_r}{\lambda_a} \right)^{\lambda_a/\lambda_r - \lambda_a} \quad (3.17)$$

σ is defined as the center-to-center distance of two touching spherical particles. C is a scale factor that re-scales the maximum depth of the potential well to ϵ . Repulsive exponent λ_r controls the hardness of the repulsion force, and attractive exponent λ_a determines the decay of the attractive tail.

The Mie potential offers a versatile framework for modeling a broad spectrum of intermolecular forces, incorporating both repulsive and attractive components to characterize interactions. The functional form of the Mie potential allows for

adjustments to accommodate specific force types, tailoring the model to the characteristics of the studied fluid. This adaptability makes the Mie potential a potent tool in molecular modeling, particularly when coupled with the statistical associating fluid theory (SAFT).¹²³ Lafitte et al.¹²⁴ first applied Mie potentials in connection with SAFT, and later, a group contribution method for associating chain molecules based on SAFT, known as SAFT- γ ,¹²⁵ was developed. SAFT- γ is widely employed in simulating molecular fluids using coarse-grained Mie models, and the SAFT- γ equation of state (EoS) is extensively used to estimate adsorbed thermodynamic properties from bulk properties. One significant advantage of using the EoS over direct simulations is the ability to quickly determine fugacity and chemical potentials from the bulk pressure. This approach significantly accelerates the research in this thesis, especially for complex systems requiring repetitive simulations under varying conditions. Furthermore, using the SAFT- γ EoS eliminates the fluctuation between simulations, enhancing reproducibility.

A well-known instance of the Mie potential arises when $\lambda_r = 12$ and $\lambda_r = 6$, commonly known as the Lennard-Jones potential.¹²⁶ The selection of the repulsive exponent 12 was somewhat arbitrary but contributes to computational efficiency.¹²⁷ This particular potential, often referred to as the LJ potential, is favored in research due to its simplicity. It is a straightforward mathematical function that quantitatively describes the potential energy of an isotropic fluid. Consequently, the LJ model has gained widespread use in scientific literature and serves as a benchmark in the field.

$$u^{LJ}(r) = 4\epsilon \left[\left(\frac{\sigma}{r} \right)^{12} - \left(\frac{\sigma}{r} \right)^6 \right] \quad (3.18)$$

The Mie potential offers more flexibility as compared to the LJ model on account of the inclusion of additional parameters. This flexibility proves advantageous, particularly when parameterizing potentials for polar molecules. A study conducted by Potoff et al.¹²⁸ revealed that the Mie potential is more accurate in describing the phase behavior of n-alkane systems. They pointed out that attempting to parameterize these systems using the LJ potential often results in a failure to simultaneously capture vapor pressure

and vapor-liquid equilibrium (VLE) curves accurately. Moreover, the Mie potential has been shown to be more successful in calculating second derivative properties. These findings underscore the advantages of using the Mie potential over the LJ potential, especially when dealing with complex molecular systems.¹²⁹

For multicomponent systems, the following Lafitte et al¹³⁰ combining rules are applied:

$$\begin{aligned}\sigma_{ij} &= \frac{1}{2}(\sigma_{ii} + \sigma_{jj}) \\ (\lambda_{ij} - 3) &= \sqrt{(\lambda_{ii} - 3)(\lambda_{jj} - 3)} \\ \varepsilon_{ij} &= \frac{(\sigma_{ii}^3 \sigma_{jj}^3)^{1/2}}{\sigma_{ij}^3} \sqrt{\varepsilon_{ii} \varepsilon_{jj}}\end{aligned}\tag{3.19}$$

Where $_{ii}$ and $_{jj}$ refer to the self parameters.

3.2 Simulation techniques

Before the age of digital computing, calculating the trajectory of numerous particles was no doubt a tedious task. However, researchers were undeterred by the immense workload. An example of such dedication is seen in the work of William Anderson, one of Lord Kelvin's research assistants, who spent over a year performing manual calculations for 5000 random collisions within a system.¹³¹ Despite the laborious nature of this work, Anderson's efforts yielded valuable insights. Nevertheless, it became evident that a faster and more efficient calculation method was desperately needed.

With the advent of computing engines, the significant value of computer simulations became apparent, leading to numerous breakthroughs in the field. Computer simulations, by providing detailed trajectories for each particle, enable the calculation of instantaneous thermodynamic properties across various microstates, which can then be averaged to determine macroscopic properties. Today, a task that took Anderson over a year to complete can be executed in a matter of milliseconds, making computer simulations a common and essential tool for validating and analyzing theoretical models. This is particularly true in cases where conducting

dangerous experimental conditions would be impractical or unsafe.

The two most common simulation techniques are Monte Carlo (MC) simulation and Molecular Dynamics (MD) simulation. The former is a stochastic approach that determines the state of a system based on the occurrence possibility, while the latter is a deterministic approach that uses Newton's law to compute the exact trajectory of a particle.^{132, 133} Although Monte Carlo (MC) simulations and Molecular Dynamics (MD) simulations yield the same averaged results under the same thermodynamic constraints, MD simulations can track fluid trajectories, making them valuable for studying transport properties.¹³⁴ Additionally, the use of parallel computing can significantly reduce the time required for large-scale MD simulations. Detailed information about the simulation methods and their variations used in this thesis will be covered.

3.2.1 Monte Carlo method

The system's total energy is a function dependent on the positions of all particles (configurational part) and the momenta of all particles (kinetic part), collectively constituting the system's phase space. Although this function is complex for a dynamic system, it exhibits preferred states that align with the system's natural tendency to minimize energy. Monte Carlo simulation is a stochastic method that plays a crucial role in capturing the microscopic structure of a system through its force field. This involves sampling the system's phase space and identifying the preferred states to deduce thermodynamic observables.¹³⁵

Sampling in molecular simulations involves random evolutions of the system's configuration, where acceptance or rejection is determined by the Boltzmann factor $\exp\left(-\frac{\Delta U}{k_B T}\right)$, with ΔU representing the difference in potential energy between the new and former configurations. Conversely, if the probability of the new state is lower, a random number is drawn from a uniform distribution between 0 and 1. The new state is only accepted if the Boltzmann factor surpasses this randomly drawn number. This method, known as importance sampling,¹³⁶ narrows down the phase space to a specific area of interest, enhancing the efficiency of the simulation.

Typically, Monte Carlo simulations are carried out in the Canonical ensemble (NVT), maintaining a constant number of particles, volume, and temperature. Random evolutions manifest as random displacements of particles. Adjusting these random moves and weighing factors allows for sampling different ensembles, such as NPT , which is achieved by making small random changes to the system's volume.¹³⁷

The Grand Canonical ensemble is distinguished for facilitating simulations with constant temperature, volume, and chemical potential.¹³⁸ Such simulations prove valuable for acquiring adsorption properties, aiding in the determination of thermodynamic factors.¹³⁶ In this context, random insertions and deletions of particles become additional necessary moves. These random moves can exhibit high flexibility; for example, parts of a chain molecule can be deleted from one end and grown back at other ends. This feature renders Monte Carlo particularly useful for equilibrating systems involving polymers. While the Monte Carlo method is efficient in evaluating ensemble averages, it lacks information about the system's dynamics.

3.2.2 Molecular Dynamics Method

Molecular dynamics is a deterministic method that produces the temporal evolution of a system. Fluid particles are treated as mechanical objects and their trajectory is governed by Newton's equation of motion.^{132,133} MD simulations solve those equations to enable dynamic analysis in a frame-by-frame manner. As the system evolves, the net force experienced by a particle i is linked to its acceleration:

$$a_i(t) = \frac{d^2 r_i(t)}{dt^2} = \frac{1}{m_i} \left(\sum_{j \neq i}^N F_{ij}(r_{ij}(t)) + E \right) \quad (3.20)$$

where $a_i(t)$ is the acceleration of particle i at time t , $r_i(t)$ is the position of particle i at time t , m_i is the mass of the particle. $\sum_{j \neq i}^N F_{ij}(r_{ij}(t))$ is the sum of the pairwise intermolecular force between particle i and other particles, obtained by taking the derivative of the inter-molecular potential. Typically a cut-off radius is implemented to ignore long-distance interactions as they become negligible. E is the external force.

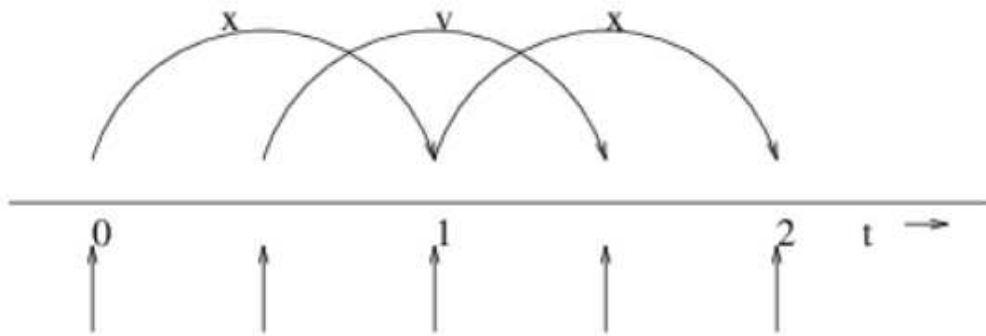


Figure 3.2: The Leap-Frog integration method, named for the distinctive manner in which positions (r) and velocities (v) alternate, resembling the leaping motion of frogs over each other's backs.¹⁴⁰

Because velocity and position are time derivatives of acceleration, system dynamics can be computed by integrating the coupled equation of 3.20 and 3.15. One way to achieve this is using leap-frog algorithm, which uses positions r at time t and velocities v at time $t - \frac{1}{2}\delta t$; It updates positions and velocities using the forces $F(t)$ determined by the positions at time t using the following relations.¹³⁹

$$v(t + \delta t) = v(t - \frac{1}{2}\delta t) + \frac{\delta t}{m}F(t) \quad (3.21)$$

$$r(t + \delta t) = r(t) + \delta t v(t + \frac{1}{2}\delta t) \quad (3.22)$$

3.2.3 Non-equilibrium molecular dynamics

NEMD simulations focus on systems that are away from thermodynamic equilibrium, where there is a gradient or time-dependent variation in a macroscopic property like temperature, pressure, or concentration. It deliberately introduces external forces, constraints, or gradients to create and maintain non-equilibrium states in the system. Here we provide a summary of several noteworthy NEMD methods.

Gradient Relaxation

One of the simplest forms of non-equilibrium molecular dynamics (NEMD) is the gradient relaxation molecular dynamics (GRMD) method, which was suggested by Maginn et al.²⁶ GRMD is a transient approach that involves setting up a non-equilibrium condition and observing its relaxation in time. In a nutshell, the simulation begins with a non-uniform concentration profile, and transport diffusivity is calculated by fitting the relaxation of the concentration profile with the observable flux.

GRMD are easy to set up and can provide insights into important transport properties. However, they often suffer from poor statistical reliability because it can be challenging to determine whether the simulation occurs in a linear response regime, especially when significant differences exist in the initial conditions.

Dual Control Volume GCMD

One of the most common non-equilibrium steady state methods is the dual control volume grand canonical molecular dynamics (DCV-GCMD) that has been used to measure transport diffusivities of pure fluids^{19,56,141–143} and mixtures.^{144,145} DCV-GCMD combines insertion and deletion methods of grand-canonical MC with MD so that particles can be deleted downstream of the pore and inserted upstream to create a steady state chemical potential, and density, gradient across the pore. The combination of MC with MD has clear advantages, as a steady state gradient can be achieved and the pressures upstream and downstream can be clearly defined. However, the use of both MC and MD moves can be cumbersome with particle insertions being particularly difficult for high pressures and dense fluids.

DCV-GCMD is particularly useful for studying diffusive flow in response to differences in chemical potential, and its ability to maintain a non-equilibrium condition in steady states provides results with greater statistical reliability. However, this method faces challenges when trying to insert chain molecules into dense fluids, and it may introduce inauthentic dynamics due to the particle insertion and deletion

process.

External Force methods

The External Force Non-Equilibrium Molecular Dynamics (EF-NEMD) method, introduced by Evans and Morris in 1984,¹⁴⁶ was among the earliest methods in this category. However, its widespread use faced challenges due to computational limitations, primarily arising from the need for relatively large systems to generate reliable results. The approach itself adheres to the general principles of non-equilibrium thermodynamics and is conceptually straightforward. In this method, an equilibrated molecular dynamics sample is perturbed from equilibrium by the application of a weak external force field to all or part of the fluid particles. This external field induces an additional acceleration in a specific direction, thereby generating a macroscopic flux in the same direction.¹⁴⁷ It is worth noting that the average fluid velocity will increase indefinitely if unsupervised, hence an effective thermostat must be employed to maintain isothermal conditions. The EF-NEMD method has been successfully used to study pure systems^{19,26} and binary mixtures.^{148–150} A similar method of using walls to push fluid particles through pores in a piston-like fashion has also been proposed by Wang et al.^{47,151}

Boundary Driven

The Boundary-Driven Non-Equilibrium Molecular Dynamics (BD-NEMD) of Frentrop et al.²⁵ is a unique method of measuring transport diffusivities where MD is solely used to induce steady state density gradients across nanopores, and stands as the primary method employed throughout this document. A representation of the method is shown in Figure 3.3. A thin region at the periodic boundary is employed to accelerate particles that happen to be in that region, which generates a flux in the z direction. The fluid accumulates at the pore entrance, resulting in a pressurised region in one of the reservoirs. Due to the conservation of mass, the fluid density on the right decreases and the resulting density gradient pushes fluid through the pore. Given a moderate force

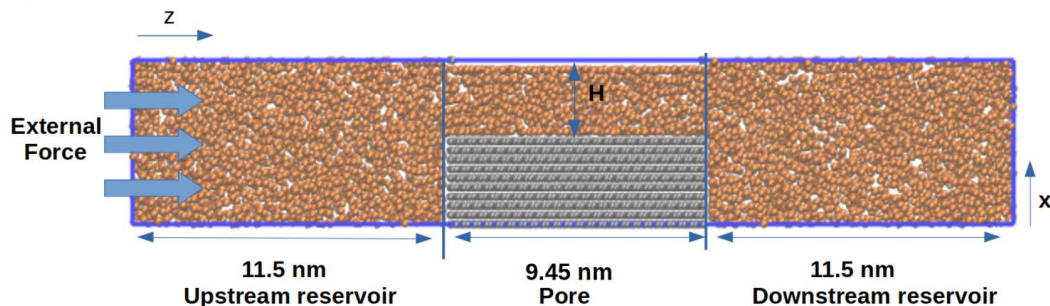


Figure 3.3: Snapshot from a boundary-driven non-equilibrium molecular dynamics (BD-NEMD) simulation applied to a slit graphene pore. An external acceleration is applied only at a small region at the periodic boundary far from the pore, leading to a density gradient and net flux across the pore. Transport diffusivity is calculated once the system reaches a steady state.

field strength, a steady state density gradient develops across the pore, and a uniform density profile will form at the bulk.

The efficacy of BD-NEMD for measuring the transport diffusivity of pure fluid and mixtures has been reported previously.^{19,25} Compared to EF-NEMD, BD-NEMD avoids the direct interference of the dynamics at the region of interest, which is key when studying transport in confined media.^{152,153} Within this document, thermostats were only applied to the solids to minimise the effect of temperature coupling on dynamics.

3.3 Transport properties from Molecular Simulations

Transport properties are predominantly computed through Molecular Dynamics (MD) simulations, offering a dynamic view of the microscopic ensemble's evolution over time. The subsequent discussion elucidates the equilibrium method for deriving various forms of diffusion coefficients from Molecular Dynamics simulations. This is followed by an exploration of diverse methodologies for extracting diffusion coefficients from non-equilibrium Molecular Dynamics simulations. Notably, these methodologies often deviate from the Green-Kubo formalism.

3.3.1 Transport under Equilibrium: Benchmark Case

In molecular simulations, a common practice to measure self-diffusion is to track the motion of individually tagged particles of type l , and employ the Einstein relation:¹³¹

$$D_{s,l} = \frac{1}{2dN_l} \lim_{\Delta t \rightarrow \infty} \frac{1}{\Delta t} \left\langle \sum_{i=0}^{N_l} |\mathbf{r}_{l,i}(t + \Delta t) - \mathbf{r}_{l,i}(t)|^2 \right\rangle \quad (3.23)$$

Where $\mathbf{r}_{l,i}$ is the vector describing the position of the i th particle of molecular type l , N_l is the total number of molecules of type l , and d is the dimension of the vector $\mathbf{r}_{l,i}$. In bulk, d has a value of 3 as particles can move in all three dimensions. However inside porous materials, the value of d can range from one to three, depending on the dimensions where particles can freely move. The angle brackets refer to an ensemble average.

Although self-diffusivity is informative in describing the motion of individual particles, it does not describe the *collective mobility* of molecules, i.e. how the collective (centre of mass) motion of molecules of type l is related to the collective motion of all molecules of type m . Given that flow in porous materials is a consequence of the collective motion of molecules, self-diffusivity cannot be used to calculate transport of fluids apart from extremely dilute systems where particles do not experience strong intermolecular forces and thus move independently.¹⁵⁴ A more general equation is thus used to describe the transport of particles of type l , influenced by the collective motion of particles of type m , denoted by Λ_{lm} .^{26,155,156}

$$\Lambda_{lm} = \frac{1}{2d} \lim_{\Delta t \rightarrow \infty} \frac{1}{\Delta t} \frac{1}{N_m} \left\langle \left(\sum_{i=0}^{N_l} \mathbf{r}_{l,i}(t + \Delta t) - \mathbf{r}_{l,i}(t) \right) \cdot \left(\sum_{j=0}^{N_m} \mathbf{r}_{m,j}(t + \Delta t) - \mathbf{r}_{m,j}(t) \right) \right\rangle \quad (3.24)$$

For a pure component system, Λ_{ll} corresponds to the Maxwell-Stefan (MS) diffusivity, $\mathcal{D}_{MS}$, also known as the collective, or Darken corrected, diffusivity, D^c . Thus Equation 3.24 can be simplified for a pure component system:

$$\Lambda_{ll} = D^c = \mathcal{D}_{MS} = \frac{1}{2d} \lim_{\Delta t \rightarrow \infty} \frac{1}{\Delta t} \frac{1}{N_l} \left\langle \left(\sum_{i=0}^{N_l} \mathbf{r}_{l,i}(t + \Delta t) - \mathbf{r}_{l,i}(t) \right)^2 \right\rangle \quad (3.25)$$

For multicomponent mixtures, elements of the matrix $[\Lambda]$ are related, but not identical to the exchange coefficients of the M-S diffusivity. Λ_{ij} provides an indirect route to calculating transport diffusivities of multicomponent mixtures (Equation 3.33). In addition to the Einstein relation, Λ_{ij} can also be measured using Green-Kubo relations which use velocities instead of displacements.²¹ Although very commonly used, calculating collective diffusivities using equilibrium molecular dynamics simulations requires many independent simulations (or one very long simulation) to get acceptable statistics.^{154, 157, 158} This renders this method laborious and computationally inefficient.

Moreover, in order to compute transport diffusivities from equilibrium simulations, additional information is required in the form of the adsorption isotherms for the fluid in the porous material. While the equilibrium methods are accepted as the *de facto* “gold standard”,¹⁵⁹ they are computationally inefficient. It is in this space that non-equilibrium models can be an alternative to calculate transport diffusivities.

In the next section we will discuss an implementation of a boundary-driven non-equilibrium method to binary mixtures and the relationship between the transport coefficients obtained as compared to those derived from other routes.

3.3.2 Transport under Non-Equilibrium

Transport diffusivity, D^t , is the mass transport coefficient used in the continuity and Fick’s equations, relating the flux of a given species, i , in a porous medium to its concentration gradient:^{148, 160, 161}

$$\mathbf{J} = -[\mathbf{D}_{ij}^t] \nabla \rho \quad (3.26)$$

Here $\mathbf{J}$ is the $n \times 1$ vector of fluxes of n components inside the pores, $[\mathbf{D}^t]$ is the $n \times n$ Fick or transport diffusion matrix, and $\nabla \rho$ is the $n \times 1$ vector of density gradients. It is important to note that fluxes need to be measured relative to a specified frame of reference which is the porous solid and is assumed to be stationary. Moreover, it is also

important to mention that $\nabla\rho$ corresponds to the density gradient of the fluid inside the porous media, i.e. the density of the adsorbate.

For a binary mixture where the flux is measured in one direction, z , the above equation can be written as:¹⁶²

$$\begin{bmatrix} J_1 \\ J_2 \end{bmatrix} = - \begin{bmatrix} D'_{11} & D'_{12} \\ D'_{21} & D'_{22} \end{bmatrix} \begin{bmatrix} \partial\rho_1/\partial z \\ \partial\rho_2/\partial z \end{bmatrix} \quad (3.27)$$

Where D'_{ii} is the self transport diffusivity, i.e. the contribution to the flux of species i due to its own concentration gradient, and D'_{ij} is the mutual diffusivity, corresponding to the contribution to the flux of species i due to the concentration gradient of species j . For a binary mixture, none of the elements of the transport diffusivity matrix are necessarily similar to each other, i.e. $D'_{ij} \neq D'_{ji}$.

Crucially, a concentration gradient is not the only source of mass flux, e.g. the Soret effect¹⁶³ describes the flux of mass driven by a thermal gradient, which have been studied in bulk^{163, 164} and under confinement^{165–167} using simulations. Similarly, consider a system in vapor-liquid equilibrium where there is a clear gradient in density, however there is no net mass flux across the interface. As an alternative to the incongruities of the Fickian formulation, Onsager's treatment provides a fundamental starting point relating the fluxes to the underlying mass transport driving force. In an isothermal case, one could relate the fluxes to the gradients of the chemical potential difference of each species, $\nabla\mu$.¹²

$$\mathbf{J} = -[\mathbf{L}] \nabla\mu \quad (3.28)$$

Here, $[\mathbf{L}]$ is the symmetric matrix of Onsager coefficients (phenomenological coefficients). An interesting inference of the Onsager treatment is that the flux of species i becomes dependent on the chemical potential gradient of both components i and j . There is an explicit recognition within this formulation that there are cross-component effects, i.e. that the flux of one component may have an impact on

the flow characteristics of the other. In particular, the cross coefficient terms become important as the density of the system becomes liquid-like and correlation effects are strong.¹⁶⁸ For a binary mixture:

$$\begin{bmatrix} J_1 \\ J_2 \end{bmatrix} = - \begin{bmatrix} L_{11} & L_{12} \\ L_{21} & L_{22} \end{bmatrix} \begin{bmatrix} \partial\mu_1/\partial z \\ \partial\mu_2/\partial z \end{bmatrix} \quad (3.29)$$

where, given that $[L]$ is symmetric:

$$L_{12} = L_{21} \quad (3.30)$$

which is not true for mutual transport diffusivities. The matrix $[\Lambda]$ with elements Λ_{ij} (Equation 3.24) is directly related to the Onsager matrix $[L]$. One can redefine the transport coefficients for a binary fluid system flowing through a porous media as follows:¹⁶⁸

$$\begin{bmatrix} J_1 \\ J_2 \end{bmatrix} = -\beta \begin{bmatrix} \Lambda_{11} & \Lambda_{12} \\ \Lambda_{21} & \Lambda_{22} \end{bmatrix} \begin{bmatrix} \rho_1 & 0 \\ 0 & \rho_2 \end{bmatrix} \begin{bmatrix} \partial\mu_1/\partial z \\ \partial\mu_2/\partial z \end{bmatrix} \quad (3.31)$$

where β is $1/RT$ where R is the gas constant and T is the temperature. Commensurate with Equation 3.27, ρ_i is the density of the adsorbed fluid. Note that the Onsager coefficients, L_{ij} , do not have the units of *length²/time* customary to describing transport, while the modified term Λ_{ij} has the same units as both transport and self-diffusivities. Going a step further, and using the Jacobian matrix for a chain of variables, Equation 3.31 can be modified so that the driving force is given in terms of the adsorbed density gradients:

$$\begin{bmatrix} J_1 \\ J_2 \end{bmatrix} = -\beta \begin{bmatrix} \Lambda_{11} & \Lambda_{12} \\ \Lambda_{21} & \Lambda_{22} \end{bmatrix} \begin{bmatrix} \rho_1 & 0 \\ 0 & \rho_2 \end{bmatrix} \begin{bmatrix} \partial\mu_1/\partial\rho_1 & \partial\mu_1/\partial\rho_2 \\ \partial\mu_2/\partial\rho_1 & \partial\mu_2/\partial\rho_2 \end{bmatrix} \begin{bmatrix} \partial\rho_1/\partial z \\ \partial\rho_2/\partial z \end{bmatrix} \quad (3.32)$$

Comparing Equation 3.27 with Equations 3.29 and Equation 3.32, the relationship

between the diffusion coefficients may be expressed as:

$$D_{ij}^t = \sum_{k=1}^{\# \text{ Comps}} \Lambda_{ik} \beta \rho_k \frac{\partial \mu_k}{\partial \rho_j} = \sum_{k=1}^{\# \text{ Comps}} L_{ik} \frac{\partial \mu_k}{\partial \rho_j} \quad (3.33)$$

and

$$\Lambda_{ij} = \frac{L_{ij}}{\beta \rho_j} \quad \rho_j \Lambda_{ij} = \rho_i \Lambda_{ji} \quad (3.34)$$

Where $\# \text{ Comps}$ is the number of components. The term $\beta \rho_i \partial \mu_i / \partial \rho_j$ is commonly known as the Darken factor, Γ_{ij} and for a pure system, it is the proportionality constant relating transport to the collective diffusivity:

$$D_{ij}^t = \sum_{k=1}^{\# \text{ Comps}} \beta \rho_k \frac{\partial \mu_k}{\partial \rho_j} \Lambda_{ik} = \sum_{k=1}^{\# \text{ Comps}} \rho_k \frac{\partial \ln f_k}{\partial \rho_j} \Lambda_{ik} = \sum_{k=1}^{\# \text{ Comps}} \Gamma_{kj} \Lambda_{ik} \quad (3.35)$$

The Darken factor can be calculated from adsorption isotherms obtained from simulations or experimental data.

3.3.3 Transport Property from BD-NEMD

Given a density gradient inside a pore and an appreciable flux, it is possible to directly assess the transport diffusivity of a fluid flowing inside a pore. To induce such gradient, we revisit the proposal of Frentrup et al.²⁵ as applied to pure fluids, modifying key assumptions, and extending it to multicomponent mixtures. First, a simulation box composed of two bulk reservoirs in contact with the pore is set up. Fluid particles are added until a target global density is reached and the system is left to equilibrate. An external field is then applied in a small section of the simulation box, which within this thesis is 2 nm wide, far enough from the pore. This region is also the boundary of the two reservoirs. This external field exerts a directional force on all particles within the small region, pushing particles at the boundary of the two reservoirs to one side, thus increasing the concentration of the fluid in one reservoir, and depleting the amount of fluid in the other. The external force is applied far away from the pore to minimise its effects on the flow across the pore, and to ensure that the

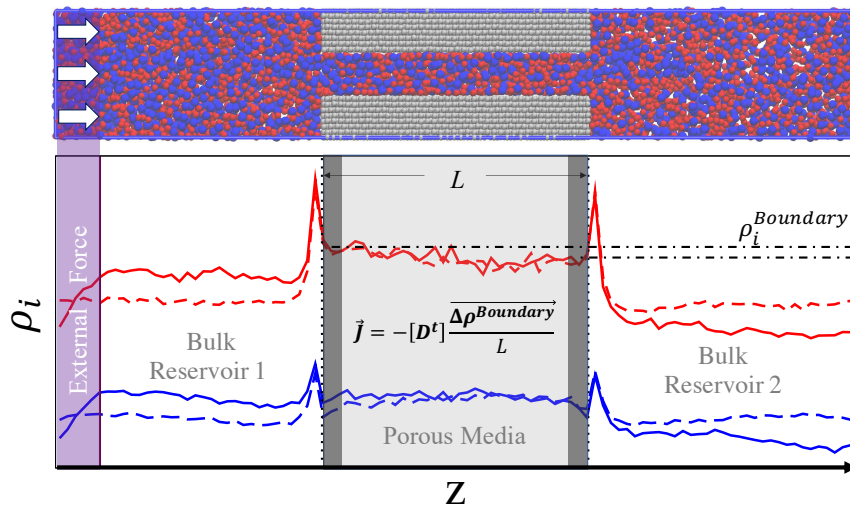


Figure 3.4: BD-NEMD method employed, as applied to a binary mixture. *Top* A snapshot from the simulation, indicating the direction of flow, with different fluid species colored red or blue and the fixed pore colored gray. Arrows denote the regions where an external acceleration is imposed. Periodic boundary conditions is employed between left and right reservoirs. *Bottom* The concentration profile of each species is colour matched with the simulation snapshot. Dashed lines correspond to systems with no external forces, and solid lines are the steady state result after applying external forces resulting in concentration gradients across the pore. Pore boundary regions are assumed to be in local equilibrium with neighboring bulk regions. The spike and trough in fluid density near the pore edge are artifacts from density rescaling of the adsorbed fluid.

flow is being induced by the density gradient across the pore. The system eventually reaches steady state, and a steady state concentration gradient occurs within the pore. This is illustrated in Figure 3.4 for a binary mixture. In terms of implementation, the directional force is the result of applying an acceleration to the particles.

Interestingly, in this method there are two bulk regions on each side of the pore. For small applied forces, the density of each bulk region remains fairly constant and the observed density gradient is only within the pore. Applying different external forces to the boundary leads to different bulk compositions and different density gradients across pores, as can be seen in Figure 3.5, for a pure fluid flowing through a slit pore.

In Figure 3.5 (Left), different forces are applied to the fluid and a density gradient develops within the pore. It can be clearly observed that the density in the adsorbed phase and in the bulk are very different. This implies that density gradients across the pore, and consequently transport diffusivities, are different depending on which density

(bulk or adsorbed) is used. It is important to mention that commonly in literature using BD-NEMD transport coefficients are calculated using reservoir densities^{25, 28, 30, 169, 170} which is only rigorous if the adsorbed densities are the same as bulk densities, i.e. for non-adsorbing systems. As will be shown later in Chapter 4, an incorrect choice leads to significant discrepancy between measurements of transport diffusivities using EqMD and NEMD.

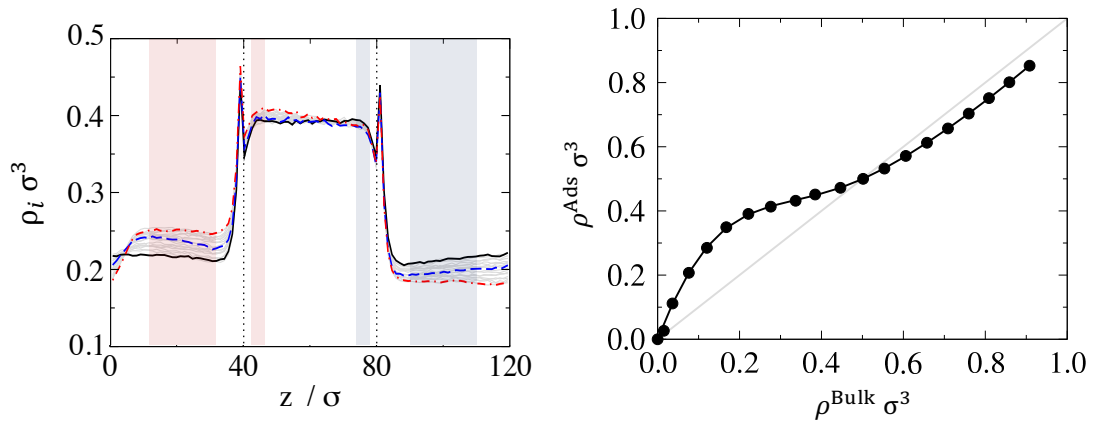


Figure 3.5: *Left* Example of a LJ fluid in a FCC pore, ρ vs z using 20 different forces. All cases are plotted grey, except three, no force (black solid), highest force (red dashed and dotted), medium force (blue dashed). It can be clearly observed that the density in the adsorbed phase and in the bulk are very different. *Right* Adsorbed vs bulk densities of the same system used to estimate the adsorbed densities at the boundaries of the pore. Errors are within the size of the symbols.

Therefore, a key consideration of the BD-NEMD method implemented in this work is to use density gradients inside the pore instead of calculating the density gradients using bulk (reservoir) concentrations. This can be particularly challenging, as the statistics inside the pore can be poor. In order to estimate the density gradients more robustly, an assumption is made that inside the pore (pore entrance and exit), the boundaries are at local equilibrium with the bulk immediate reservoirs, thus the amount adsorbed at the boundaries can be calculated from equilibrium simulations of a bulk region. Knowing the bulk densities on each side, the adsorbed density at the boundary inside the pore can be estimated, and the density gradient is calculated. An example of the such relationship between bulk and adsorbed density can be seen in Figure 3.5 (Right).

Once the density gradient is calculated, the flux of each component, J_i , is calculated in the middle of the pore:

$$J_i = \frac{N_i^+ - N_i^-}{A_{xy} t_{run}} \quad (3.36)$$

Where A_{xy} is the area of the plane in the pore perpendicular to the direction of the flow. t_{run} is the total simulation running time and N_i^+ and N_i^- are the total number of particles of species i that have passed the middle of the pore in the same and opposite direction to the direction of the external force respectively. The choice of the middle of the pore is arbitrary if the cross-sectional area of the pore does not change.

By running simulations with different forces, one could obtain different density gradients and fluxes which can be used to improve the statistics. Transport diffusivities can be assessed using the following equation:

$$(\mathbf{D}^t)^T = -[(\partial\rho/\partial\mathbf{z})^T (\partial\rho/\partial\mathbf{z})]^{-1} [(\partial\rho/\partial\mathbf{z})^T \mathbf{J}] \quad (3.37)$$

For an m component mixture, $\mathbf{D}^t$ is the transport diffusivity matrix defined in Equation 3.27, $\partial\rho/\partial\mathbf{z}$ and $\mathbf{J}$ are $n \times m$ matrices of concentration gradients and fluxes respectively. n is the number of *in silico* experiments carried out, each with a different boundary force, and T denotes a matrix transpose. Figure 3.6 shows the linear relationship between concentration gradient and flux by borrowing data from a later chapter.

One of the benefits of using the BD-NEMD technique over other non-equilibrium approaches is the fact that the force itself is not used to evaluate transport coefficients. It is applied in a region so far away from the pore that it does not affect the transport inside the pores. However, what the force does is to help in building up fluid on one side of the pore. Transport is thus a consequence of the concentration gradient across the pore, and not the applied force.

Thus it does not strictly matter what force is applied to either species, as long as there are measurable concentration gradients and fluxes of all species across the pore. If fluxes are only functions of concentration gradients, and not applied forces, transport

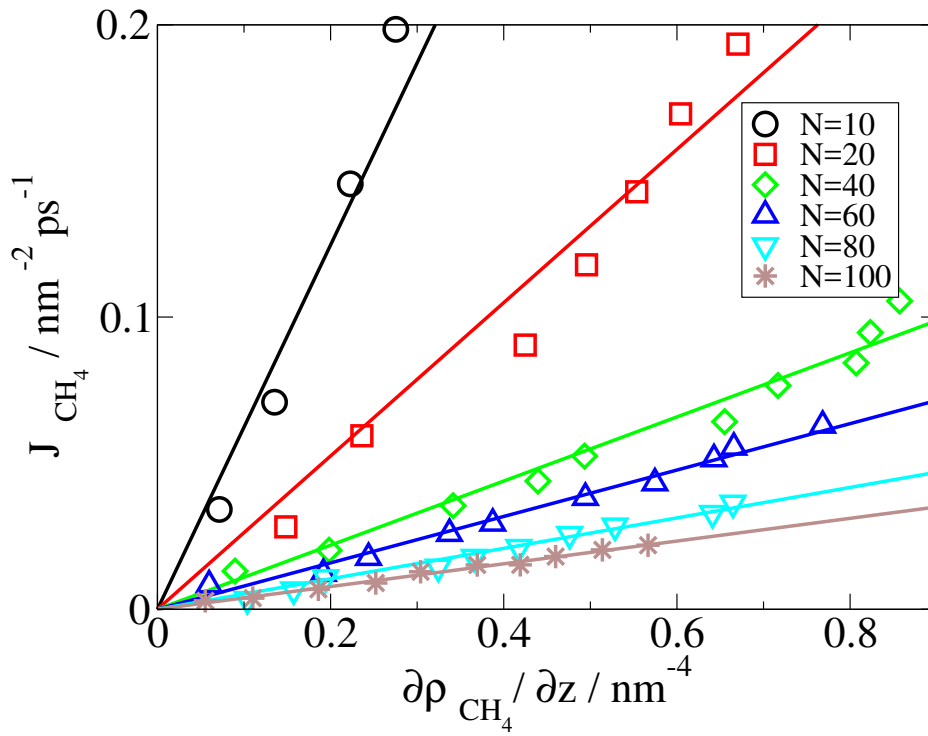


Figure 3.6: Flux, J , as a function of density gradients for pure CH_4 in coronene fragment pores. It can be seen that the relationship is highly linear.

coefficients are independent of those concentration gradients and thus different forces can be applied to any species.

This is in contrast with other NEMD techniques, such as external force NEMD, where a force is applied to all species. In that case, the applied force is directly responsible for the transport of both species and transport coefficients are calculated by relating fluxes to applied forces. In that case, if molecules have different masses, one might observe buoyancy effects and artefacts that might affect the measurement of transport coefficients. To overcome that if particles have different masses, accelerations should be modified to ensure the same force applied to different species.

Permeability

An alternative to the calculation of diffusivities is the assessment of the permeance, K , defined as:

$$J^{Total} = -K \frac{\partial P}{\partial z} \quad (3.38)$$

where J^{Total} is the total mass flux of the fluid mixture, and $\partial P/\partial z$ is the pressure gradient across the pore which was estimated by the SAFT- γ EoS, using bulk densities as input. K is commonly measured and reported in literature.²⁸

Permeance is a property of both fluid and the porous material. It is closely related to permeability (κ) which, for large pores, is an intrinsic property of the porous material only, and is given by:⁵¹

$$\kappa = K\eta/\rho^{Total} \quad (3.39)$$

where η is the dynamic viscosity of the fluid and ρ^{Total} is the total adsorbed density of the fluid inside the pore. Permeabilities are commonly reported for shales and are typically in the order of nanoDarcies (nD) at reservoir conditions.⁵¹ Moreover, given that permeabilities are, in principle, only affected by the pore geometry and not by the fluid composition and density, they can be used to quantify the extent to which mesoporous carbon pores of different rugosities can be used to represent organic shales.

To evaluate η using Equation 3.39, pure component viscosities can be calculated from bulk fluid simulations. In the case of mixtures, viscosity η_{ij} can be estimated using the Arrhenius law:¹⁷¹

$$\ln \eta_{ij} = x_i \ln \eta_i + x_j \ln \eta_j \quad (3.40)$$

where x refers to the mole fraction and subscripts i and j refer to pure component properties. This equation is applicable for ideal binary mixtures. Although a single state point is the minimum needed to obtain a value of permeability, 20 realisations, each using a different external boundary force, were employed to obtain the permeabilities using least square regression:

$$(K)^T = -[(\partial \mathbf{p}/\partial \mathbf{z})^T (\partial \mathbf{p}/\partial \mathbf{z})]^{-1} [(\partial \mathbf{p}/\partial \mathbf{z})^T \mathbf{J}^{Total}] \quad (3.41)$$

Chapter 4

Use of Boundary-Driven Nonequilibrium Molecular Dynamics for Determining Transport Diffusivities of Multicomponent Mixtures in Nanoporous Materials

4.1 Introduction

Understanding and modelling of mass transport in porous media is essential in nearly all branches of natural sciences and engineering given the ubiquity of fluid flow in natural and anthropogenic solids. Particularly in engineering applications, a significant number of processes exploit the relative differences in mass transport to separate different components of a fluid mixture.

Experimental determination of mass transport and diffusion in nanoporous materials is challenging. Although some recent techniques based on nuclear magnetic resonance seem very promising,^{116,172} a fundamental predictive theory behind

transport in nanoconfined spaces is lagging. This is mainly due to the complexities of incorporating the surface-fluid effects, which are, in many cases, dominant.¹⁷³ Thus molecular simulations can provide useful insight into the mechanism of transport and separation in confined media.

The Boundary Driven Non-Equilibrium Molecular Dynamics (BD-NEMD) method by Frentrup et al.²⁵ stands out as a distinctive approach for measuring transport diffusivities. In this method, Molecular Dynamics (MD) is exclusively employed to induce steady-state density gradients across nanopores. This is achieved by applying an external field solely to a small region in the simulation box, positioned far from the pore. While extensively utilized in the literature for both pure components^{25,27–31} and mixtures,^{32,33} the extent of agreement between transport diffusivities measured using this technique and other established methods, such as EqMD, remains unknown. Furthermore, there exist significant assumptions that require scrutiny to ensure concordance between transport diffusivities measured from BD-NEMD and EqMD under all conditions.

Additionally, although BD-NEMD has been employed for studying multicomponent mixtures,³² it has focused solely on measuring self-transport coefficients, and the impact of cross-species transport coefficients has not been explored. The values of cross-species transport coefficients have not been previously determined using BD-NEMD, leaving uncertainty about the agreement between transport diffusivities of multi-component mixtures measured using this method and those from EqMD simulations.

In this chapter, the boundary-driven molecular modelling strategy to evaluate mass transport coefficients of fluids in nanoconfined media is revisited and expanded to multicomponent mixtures. The method requires setting up a simulation with bulk fluid reservoirs upstream and downstream of a porous media. A fluid flow is induced by applying an external force at the periodic boundary between the upstream and downstream reservoirs. The relationship between the resulting flow and the density gradient of the adsorbed fluid at the entrance/exit of the porous media provides for a

direct path for the calculation of the transport diffusivities. It is shown how the transport diffusivities found this way relate to the collective, Onsager and self-diffusion coefficients, typically used in other contexts to describe fluid flow in porous media. Examples are provided by calculating the diffusion coefficients of: a Lennard-Jones (LJ) fluid and mixtures of different-size LJ particles in slit pores; a realistic model of methane in carbon-based slit pores, and binary mixtures of methane with hypothetical counterparts having different attractions to the solid. The method is seen to be robust and particularly suited for the study of liquid flow in nanoconfined media. The main workflow is summarised in Figure 4.1.

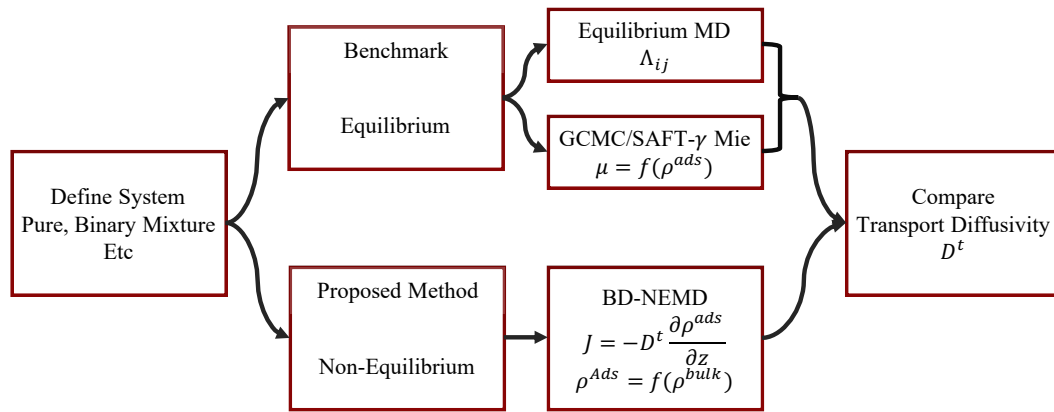


Figure 4.1: Summary of workflow employed in this article, where transport diffusivities of different systems are calculated using EqMD and BD-NEMD, and are then compared with each other.

4.2 Methodology

4.2.1 Molecular Interactions

All fluid molecules are modelled as single spheres, with the Mie potential describing intermolecular interactions between particles. Cross interactions are resolved by using the Lafitte et al combination rules.¹³⁰

4.2.2 Modelling Adsorption

As highlighted previously in Chapter 2, in the BD-NEMD method it is important to relate bulk densities to the adsorbed densities. Moreover, if one wants to calculate transport diffusivities from EqMD (Equations 3.24 and 3.35), adsorption isotherms relating adsorbed densities to chemical potentials or fugacities are essential.

To relate adsorbed densities to bulk densities, in this work both grand-canonical Monte Carlo (GCMC),^{131,174} and EqMD simulations have been used. GCMC models the pore and the bulk separately using a defined chemical potential, whereas the EqMD simultaneously models a bulk in equilibrium with the pore. For each GCMC simulation, 40,000 cycles were used, where each cycle consists of a displacement move, an insertion and a deletion. For particle displacement moves, the probability of success was set to 0.25.

To calculate chemical potentials, for this particular force field one may use directly a molecular based equation of state (EoS), SAFT- γ Mie.¹⁷⁵ The inputs of this EoS are the same as the Mie potential:

$$A^{SAFT} = f(T, \rho \mid \lambda_{ij}, \varepsilon_{ij}, \sigma_{ij}) \quad \forall i, j \quad (4.1)$$

Where A^{SAFT} is the molar Helmholtz free energy of the fluid. The correspondence between the results of the equation of state and those from molecular simulations has been discussed elsewhere.^{176–183}

An additional advantage of employing the SAFT- γ Mie EoS alongside the BD-NEMD, is that it allows accessing Λ_{ij} (Equation 3.24), given the condition that the boundaries of the pore are in equilibrium with the bulk regions:

$$\begin{aligned} (\mathbf{L})^T &= -[(\partial\mu/\partial\mathbf{z})^T (\partial\mu/\partial\mathbf{z})]^{-1} [(\partial\mu/\partial\mathbf{z})^T \mathbf{J}] \\ \Lambda_{ij} &= \frac{k_B T L_{ij}}{c_j} \end{aligned} \quad (4.2)$$

Where $\partial\mu/\partial\mathbf{z}$ is calculated using either SAFT- γ Mie EoS, or from GCMC.

Adsorption of Multicomponent Mixtures

Single component adsorption isotherms can be readily measured using simulations and experiments,¹⁸⁴ however it is more challenging to map out the adsorption isotherms of a multi-component fluid because knowledge on fluid compositions are required to get the full picture.^{185,186} In molecular simulation, generating a mapping from bulk adsorption to adsorbed adsorption involves performing simulations across a range of mixture composition and density, which can be extremely time-consuming and prone to errors. Alternatively, predicting mixture adsorption equilibria using only single-component data can significantly accelerate the research process while providing robust results. One solution that achieve this is Myers and Prausnitz's Ideal Adsorption Solution Theory (IAST), which is a widely used tool to estimate mixture adsorbed isotherm from the single-component isotherms of the constitute fluids.^{187,188} The theory is based on the assumption that the adsorbed fluid is an ideal solution in which interaction between fluid molecules are equivalent in strength.¹⁸⁹ Because this ideal adsorbed phase is equilibrated with a bulk phase, IAST can be seen as an analogy of Raoult's law which computes the adsorbed phase using bulk pressure and composition.¹⁹⁰ Methods for implementing IAST have been extensively discussed in literature.¹⁹¹ In this thesis, the IAST method is implemented using the pyIAST package by Haxrancyk et al.¹⁹²

4.2.3 Systems Studied

Four case studies are chosen in this study:

- Case I: A pure LJ fluid within a slit pore: as a validation of the proposed BD-NEMD method by comparison to transport diffusivities calculated using EqMD;
- Case II: Pure Methane within a slit pore: as an example of application to realistic fluids;
- Case III: A binary mixture of two methane-like fluids, with one having realistic

parameters (as in Case II) and the other having augmented interactions with the pore: as an example application on the effect of the solid-fluid interaction on selectivity;

- Case IV: A binary LJ mixture, where one species is the same as Case I, and the other has a radius 30 percent larger: as an example application on the effects of size differences on self and mutual diffusivities in binary mixtures

All parameters for the four systems studied are presented in Table 4.1. All walls are modelled as FCC lattices, and for all cases, the lattice constant is $a = 2\sqrt{2} \sigma^{Wall}$.

4.3 Simulation details

In all simulations, a system is set up with a solid pore of $L_z = 12$ nm positioned in the middle of a 36 nm simulation box, thus having two bulk regions on each side, each being 12 nm in length. The pore region is an FCC smooth slit pore.

Lengths of the box (and the pore) in the x and y dimensions are the same, being greater than 10σ . The large values of pore dimensions and simulation box sizes are chosen to minimise finite size effects. In particular, the ratio of particle size to pore length (σ/L) is always less than 0.05 and the ratio of pore height to pore length (H/L) is always less than 1. From previous studies,¹⁹³ it is known that these dimensions are far from those resulting in significant finite size effects.

The total void volume of the simulation box is known and fixed and particles are added to a target global fluid density. Equilibrium molecular dynamics simulation are then run in the NVT ensemble, so that the system equilibrates and adsorption isotherms can be assessed.

With the system equilibrated, the final configuration is used for two purposes. Firstly, the same system is used as the initial configuration for the BD-NEMD simulations. Secondly, the pore section of the final configuration is isolated (the bulk regions removed and periodic boundary conditions imposed in x and z directions) and used in EqMD

Table 4.1: Force-field parameters for the four cases studied.

Case I				
T = 298 K		H = 2.0 nm		
Species		Interaction Parameters		
<i>i</i>	<i>j</i>	λ_{ij}	ε_{ij}/k_B / K	σ_{ij} / nm
LJ Fluid (LJF)	LJF	12.0	200.0	0.300
LJ Wall (LJW)	LJW	12.0	200.0	0.300
LJF	LJW	12.0	200.0	0.300
$M_{w,LJ} = 40.00 \text{ g mol}^{-1}$				
Case II				
T = 298 K		H = 2.6 nm		
Species		Interaction Parameters		
<i>i</i>	<i>j</i>	λ_{ij}	ε_{ij}/k_B / K	σ_{ij} / nm
Methane (M)	M	16.4	170.8	0.375
Wall (W)	W	12.0	170.8	0.350
M	W	14.0	170.4	0.363
$M_{w,M} = 16.04 \text{ g mol}^{-1}$				
Case III				
T = 298 K		H = 2.6 nm		
Species		Interaction Parameters		
<i>i</i>	<i>j</i>	λ_{ij}	ε_{ij}/k_B / K	σ_{ij} / nm
Methane A (MA)	MA	16.4	170.8	0.375
Methane B (MB)	MB	16.4	170.8	0.375
Wall (W)	W	12.0	170.8	0.350
MA	MB	16.4	170.8	0.375
MA	W	14.0	170.4	0.363
MB	W	14.0	136.4	0.363
$M_{w,MA} = M_{w,MB} = 16.04 \text{ g mol}^{-1}$				
Case IV				
T = 298 K		H = 2.0 nm		
Species		Interaction Parameters		
<i>i</i>	<i>j</i>	λ_{ij}	ε_{ij}/k_B / K	σ_{ij} / nm
LJF-1	LJF-1	12.0	200.0	0.300
LJF-2	LJF-2	12.0	200.0	0.400
LJ Wall (LJW)	LJW	12.0	200.0	0.300
LJF-1	LJF-2	12.0	193.9	0.350
LJF-1	LJW	12.0	200.0	0.300
LJF-2	LJW	12.0	193.9	0.350
$M_{w,LJF-1} = 40.00 \text{ g mol}^{-1}$, $M_{w,LJF-2} = 94.81 \text{ g mol}^{-1}$				

simulations to calculate Λ_{ij} in an essentially infinite pore setup. EqMD and NEMD simulations are then used to calculate transport diffusivities which were compared.

Each simulation is run for 10 million time-steps of 2 fs. The first 4 ns are used for equilibration, or reaching a steady state, and the remaining 16 ns were analysed as the main production run.

For both BD-NEMD and EqMD, following previous studies,^{25,31} simulations were run in the NVT_W ensemble, where T_W refers to the temperature coupling of the solid particles only. This means that no temperature coupling is used for the fluid as to avoid influencing its dynamics, and instead energy was added or removed using wall particles as a thermostat, i.e. the excess energy input of the external force is removed by the walls. To implement this, the pore solid particles are allowed to vibrate about their equilibrium position using position restraints of the harmonic form, with a bonding potential of $10,000 \text{ kJ mol}^{-1} \text{ nm}^{-2}$ and an equilibrium bond distance of σ_{wall} . By only applying temperature coupling to the solid particles, the temperature of both solid and fluid are kept constant about the equilibrium temperature, which is illustrated in Fig 4.2. Moreover, To ensure the positions of the fluid were not modified, no centre of mass motion removal was used.

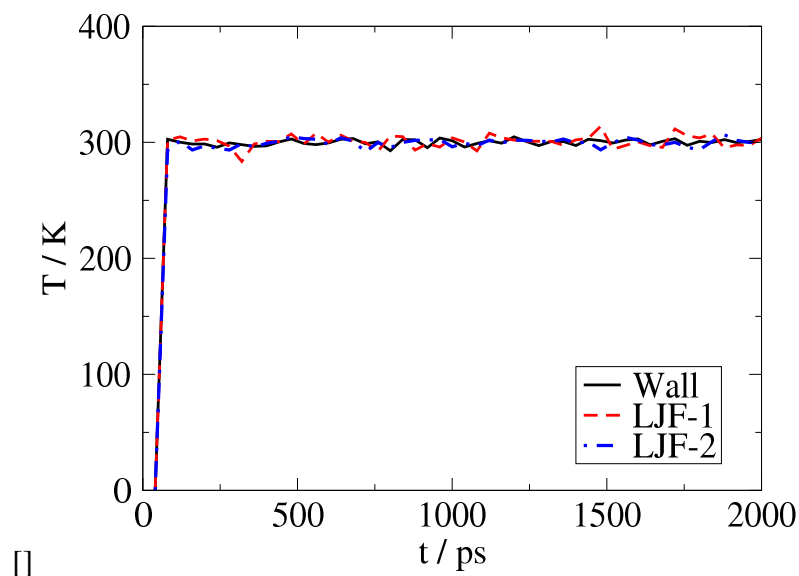


Figure 4.2: Applying thermostating to the walls keeps the fluid temperature controlled: an example of Case IV where reduce density is kept at 50 % and $x_{LJF-1} = 0.5$. An acceleration of 0.004 nm ps^{-2} is applied to both species.

BD-NEMD simulations are run using a modified version of GROMACS/5.1.2¹⁹⁴ and for each simulation at each state point, 20 different simulations were run using applied accelerations in the range 0-0.004 nm ps⁻² to keep the perturbations of the system within the "linear regime". EqMD simulations are run using GROMACS/2018¹⁹⁵ to ensure results are not subject to software bias. All visualisations of simulations have been rendered using the VMD package.¹⁹⁶

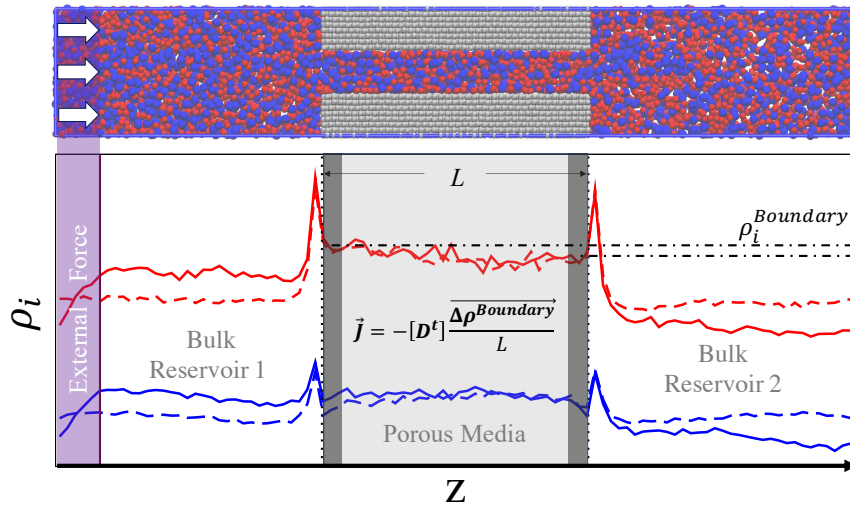


Figure 4.3: BD-NEMD method employed, as applied to a binary mixture. **Top** A snapshot from the simulation, indicating the direction of flow, with different fluid species colored red or blue and the fixed pore colored gray. Arrows denote the regions where an external acceleration is imposed. Periodic boundary conditions are employed between left and right reservoirs. **Bottom** The concentration profile of each species is colour matched with the simulation snapshot. Dashed lines correspond to systems with no external forces, and solid lines are the steady state result after applying external forces resulting in concentration gradients across the pore. Pore boundary regions are assumed to be in local equilibrium with neighboring bulk regions.

4.4 Results and Discussion

4.4.1 Case I: Pure LJ Fluid

For the pure LJ system in a slit pore of height 2 nm (6.67σ), simulations are run from the dilute limit to highly concentrated systems, i.e. $\rho\sigma^3 = 0.02$ – 0.85 at $T = 1.5 \varepsilon/k_B$, which is above the critical temperature of the LJ fluid ($T_c = 1.31 \varepsilon/k_B$).¹⁹⁷ The coexisting fluid

density at the supercritical fluid-solid transition for a bulk LJ fluid is at $\rho\sigma^3 = 1.015^{198}$ which set the upper limit of densities to 0.85, ensuring the fluid inside the pore did not undergo a phase transition to a solid phase.

Figure 4.4 shows the measured adsorbed concentrations for all bulk concentrations studied. It could be clearly seen that the pore is very selective at lower densities, while at higher densities the concentration is only around five percent less than bulk concentrations. The latter underestimation is presumably an artefact of the particular definition of the pore height used in this work.

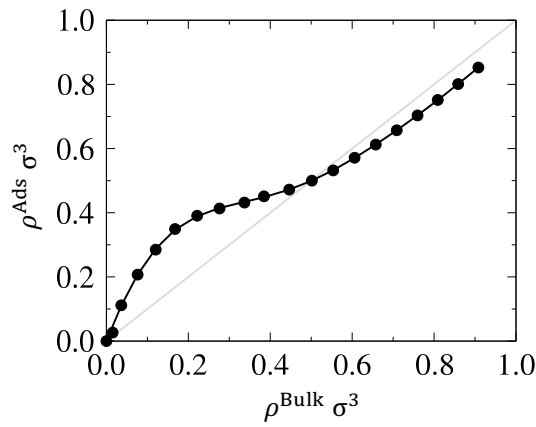


Figure 4.4: A LJ fluid at $T = 1.5 \varepsilon/k_B$, flowing through a FCC pore with pore height $H = 20/3 \sigma$, with the solid particles being the same as the fluid LJ particles. Adsorbed vs bulk densities of the same system used to estimate the adsorbed densities at the boundaries of the pore. Errors are within the size of the symbols.

Adsorption Isotherms

BD-NEMD can be used to measure both transport diffusivities (Equation 3.37) and collective diffusivities, Λ_{ij} , (Equation 4.2). While the first calculation is direct, for the latter, one needs to find the chemical potential gradients across the pore. Otherwise, Λ_{ij} can also be directly calculated using EqMD (Equation 3.24). As a test of robustness of the BD-NEMD method developed, Λ_{ij} is compared with both methods.

Furthermore, chemical potentials are required to evaluate the Darken factors so that Λ_{ij} could be used to calculate D^t (Equation 3.35). Chemical potentials are assessed using both GCMC and the SAFT- γ Mie EoS. While using the EoS, the

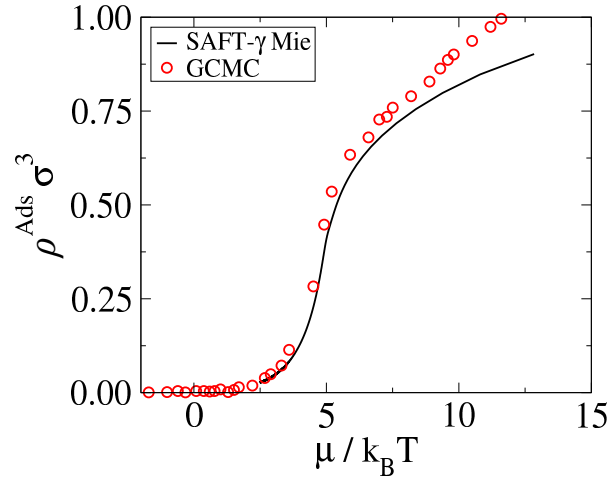


Figure 4.5: Adsorption Isotherm of Case I. The SAFT- γ Mie approach uses direct MD simulations where the pore and the adsorbed fluid are in equilibrium with the bulk, and chemical potentials are estimated using the equation of state with the bulk densities as input. Errors are within the size of the symbols.

chemical potential is calculated using the bulk density at equilibrium with the adsorbed density, whereas in GCMC (μVT ensemble) chemical potential is an input from which adsorbed densities can be determined. Although the two methods are fundamentally different to each other, a quantitative agreement between them can be seen in Figure 4.5. The disagreement at higher densities is attributed to sampling inefficiencies in GCMC. The equation of state is computationally much more efficient and thus the SAFT- γ Mie EoS is chosen as the preferred method of measuring chemical potentials, and Darken factors.

The relationship between chemical potential and adsorbed densities can be used to calculate chemical potential gradients across the pore from BD-NEMD simulations, which can then be used to determine Λ_{ij} using Equation 4.2. Additionally, the Darken correction factor is also calculated from the same relationship:

$$\Gamma_{ii} = \beta \rho_i^{\text{Ads}} \frac{\partial \mu_i}{\partial \rho_i^{\text{Ads}}} = \beta \frac{\partial \mu_i}{\partial \ln(\rho_i^{\text{Ads}})} \quad (4.3)$$

Γ_{ii} is calculated as a function of the adsorbed concentration using SAFT- γ Mie EoS and the results can be seen in Figure 4.6 (Right). The Darken factor approaches the value of 1 at infinite dilution, corresponding to the expected value for an ideal gas. As

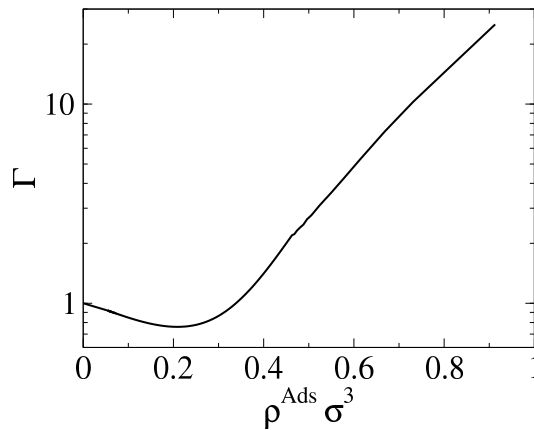


Figure 4.6: The Darken factor, Γ , vs adsorbed density, ρ^{ads} calculated from the SAFT- γ Mie EoS.

more particles are added at lower densities, the presence of attractive forces lead to a decrease in the value of the Darken factor. The Darken factor increases as further insertion of fluid particles becomes less favourable, culminating in very large increases in the chemical potential. At low densities, there is only a small layer of adsorption nearest to the surface. At high density, the pore is saturated and the fluid is highly ordered. The onset of saturation occurs at $\rho\sigma^3 = 0.4$, after which particle insertions become less favourable and the chemical potential increases.

EqMD

For each value of the density of fluid inside the slit pore, 60 independent equilibrium simulations, or 300 million time steps in total, were run. Self-diffusivities were calculated using Equation 3.23. Then, the mean square displacement (MSD) of the centre of mass of the fluid in the two dimensions (plane) parallel to the pore surface is measured as a function of time. As can be seen in Equation 3.24, in the limit of an infinite time, collective diffusivity, Λ_{ii} is given by the slope of the linear line describing MSD as a function of time. Figure 4.7 shows the results for one density ($\rho\sigma^3 = 0.5$), and although the average value of all 60 simulations is linear, each simulation has a drastically different MSD profile relative to the average, and thus the errors associated with measuring collective diffusivities can be particularly large. This is found to be true across all concentrations.

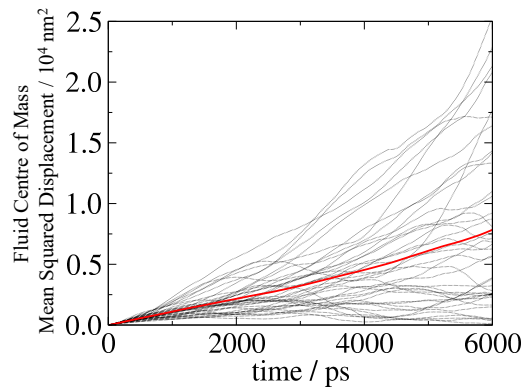


Figure 4.7: Centre of mass mean squared displacement of 60 different EqMD simulations of the same system ($\rho\sigma^3 = 0.5$). Each dotted line represents results of one simulation. The average of the 60 simulations is highlighted as the thick red line which is related to the collective diffusivity, Λ .

With the collective diffusivities measured from EqMD, and the Darken factors from adsorption isotherms, it is possible to calculate transport diffusivities, $D^t = \Gamma\Lambda$ (Equation 3.33).

NEMD

For different densities, 20 different forces are applied at the boundary and fluxes and concentration gradients are evaluated. As can be seen in Figures 4.8a and 4.8b there is a linear relationship between the applied force and the flux as well as the density gradient, i.e. the system is kept within the linear response regime. Frentrop et al.²⁵ observed a non-linear response when employing forces an order of magnitude higher than that applied in this work.

In Figures 4.8a and 4.8b, fluxes and density gradients are shown for different applied forces respectively. The symbols are colored based on the equilibrium adsorbed densities, i.e. where the force is null. Figures 4.8c and 4.8d are the contour maps of fluxes and density gradients as functions of the force and the fluid density. Although one would expect that increasing the external force leads to greater flux and density gradients, for a given applied force the value of flux (or density gradient) peaks at intermediate loadings. This could be explained by noting that at higher densities, applying a force to particles at the boundary pushes them into a dense fluid region, and

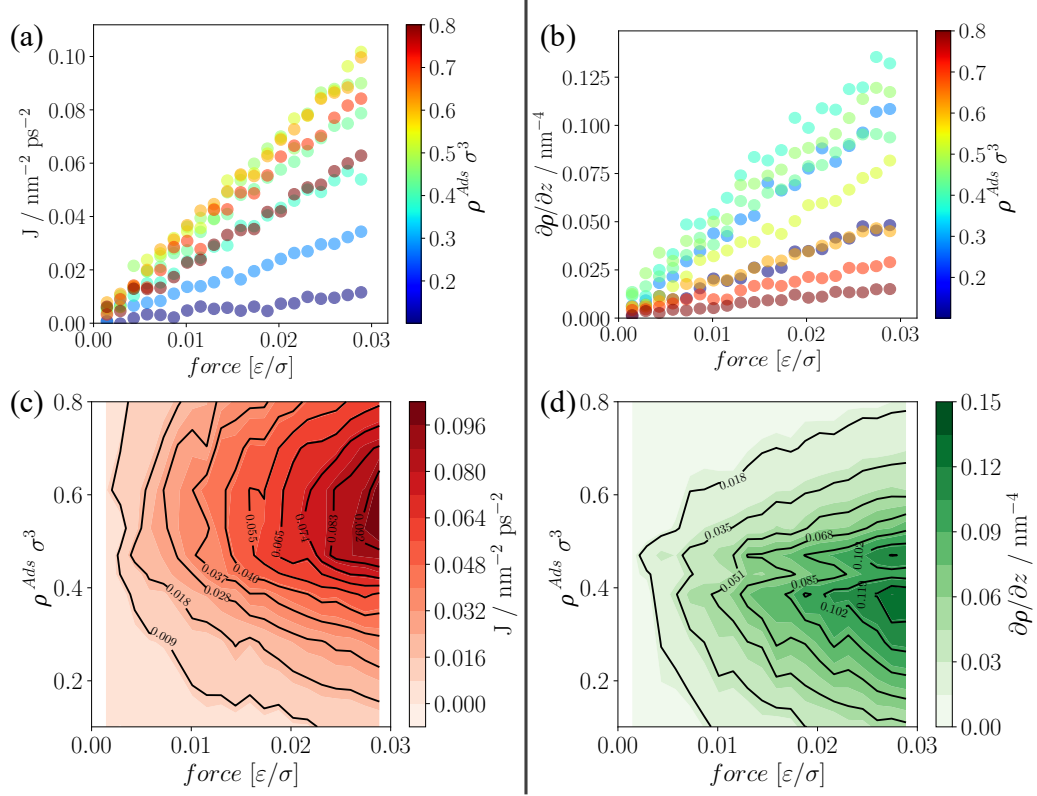


Figure 4.8: Flux, J , and density gradient, $\partial\rho/\partial z$ for fluid densities and external forces applied for the LJ fluid. **a** J vs force, and **b** $\partial\rho/\partial z$ vs force, where different colours correspond to different fluid densities at equilibrium. **c** and **d** are contour maps of fluxes and density gradients respectively, showing maxima at intermediate loadings. Errors are within the size of the symbols.

flow is hindered. However, this does not mean that the transport diffusivity is highest at intermediate concentrations. The value of flux should not be taken as an indication of faster transport. It is only by relating fluxes to density gradients where a true measure of transport is given, which can be seen in Figure 4.9. The aforementioned figure clearly highlights that increasing pore loading leads to higher transport diffusivities.

Comparison between EqMD and BD-NEMD

A summary of all transport coefficients measured using EqMD and BD-NEMD is presented in Figure 4.10. From EqMD, self-diffusivity (D^{self}) and collective diffusivity (Λ_{EqMD}) are calculated using Equations 3.23 and 3.24 respectively, and transport diffusivity (D_{EqMD}^t) is calculated using Equation 3.35, i.e. by multiplying Λ_{EqMD} by the Darken factor, Γ . From BD-NEMD, $\Lambda_{BD-NEMD}$ and $D_{BD-NEMD}^t$ were

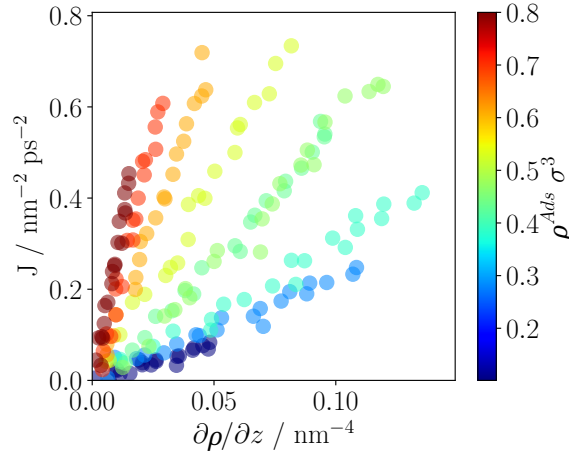


Figure 4.9: Flux, J , vs density gradient, $\partial\rho/\partial z$ for the LJ fluid. Colours indicate adsorbed density at equilibrium. The slope of each line corresponds to the transport diffusivity for the given loading (Equation 3.37). Errors are within the size of the symbols. In addition, it is worth noting that the confidence in the slope also contributes to the error in the estimation of transport diffusivity. While the uncertainty in the slope is not explicitly reported in this work, the clear linear trend observed and the substantial number of sample points indicate that this error is likely minimal.

calculated using Equations 4.2 and 3.37 respectively.

As can be seen, there is quantitative agreement between BD-NEMD and the benchmark equilibrium simulations across all densities. The BD-NEMD method captures the same trend as the EqMD simulations, however, both transport and collective diffusivities are underestimated in the non-equilibrium simulation. This underestimation is about 20 % in the value of Λ and 15 % in the value of D' . The error is greatest at lower densities which presumably caused by uncertainties in the equilibrium simulations, as the error bars are very large and the values obtained using NEMD all lie within the error associated with EqMD.

It is important to note that while the coefficients approach the same value at infinite dilution, $D_{\rho \rightarrow 0}^s = \Lambda_{\rho \rightarrow 0} = D'_{\rho \rightarrow 0} \approx 3.5 \sigma(\varepsilon/m)^2$, upon increasing densities, these coefficients show different trends. Self-diffusivity decreases with increasing densities and is roughly 20 times less at the highest density than at the infinite dilution limit, as particles in denser phases have smaller velocities and less free paths to diffuse uninterruptedly. This trend is not observed in the collective diffusivities, as the value

of Λ peaks at intermediate densities of $\rho^{Ads}\sigma^3 = 0.45$ and then slightly decreases at higher density (see Figure 4.8). Given that the Darken factor substantially increases at higher densities, transport diffusivities show the opposite trend to the self-diffusivities being up to 15 times larger at the highest density relative to the lowest. The fact that transport diffusivities can be orders of magnitude larger than self-diffusivities stems from the very significant collective motion of the fluids as a consequence of smoothness of the surface of the slit pore, and any individual movement of adsorbed molecules correlates with the movement of all other molecules in the system.

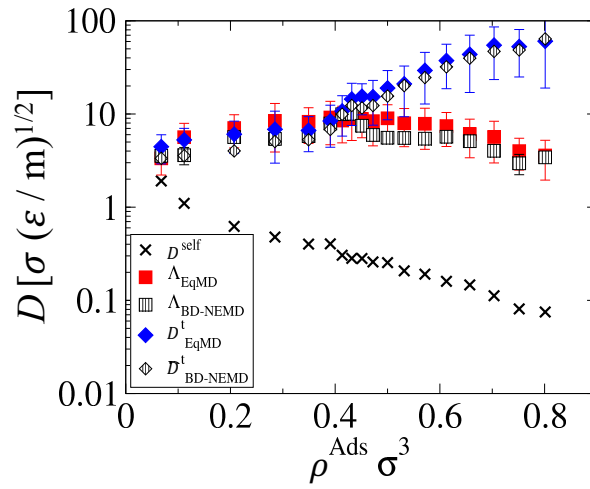


Figure 4.10: Summary of the different transport coefficients measured for the LJ system studied.

The key difference between this work and previous BD-NEMD approaches in literature is in the way density gradients are defined in the calculations of the transport diffusivities. As mentioned previously, a common practice is to use the unambiguous bulk reservoir densities. However, as can be seen in Figure 4.11, using bulk densities as the driving force for calculating transport coefficients inside the porous regions leads to drastically different profile for transport diffusivity as a function of density. Bulk density gradients do not take into account the effect of pore adsorption on transport, and/or any pore entrance effects that may be present. Using bulk density gradients leads to significant overestimation of transport diffusivity at low loadings, and underestimations at intermediate loadings, with a clear minimum at around $\rho^{Ads}\sigma^3 = 0.4$. This minimum is neither observed for the BD-NEMD developed in this

work nor the EqMD benchmark (see Figure 4.11).

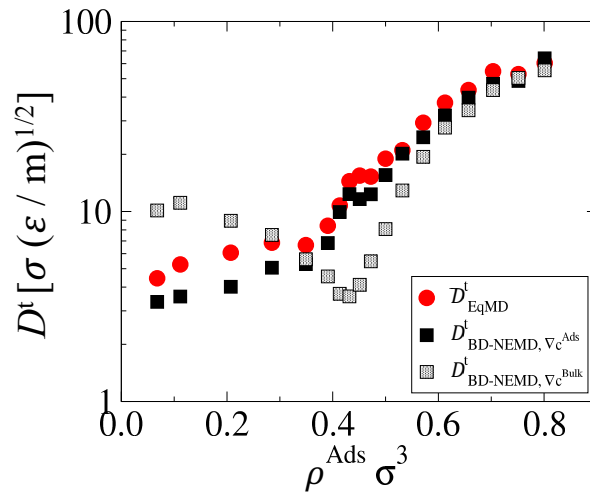


Figure 4.11: Comparison between transport diffusivities with BD-NEMD assuming the concentration gradient is given by the bulk compositions across the pore (open squares), as commonly used in literature, or if adsorbed densities are used (black squares), implemented in this work. Red squares correspond to benchmark EqMD results. Errors are within the size of the symbols.

4.4.2 Case II: Methane

To exemplify how this methodology could be employed to investigate transport of real fluids, BD-NEMD is further tested on a system consisting of supercritical methane in a slit pore at $T = 300$ K. Essentially the system resembles that of Case I but the fluid force-field can be traced back to a realistic model. The Mie parameters describing the intermolecular interactions have been previously optimized to reproduce vapor-liquid equilibrium.¹⁹⁹ The quantitative agreement between results obtained from MD with those obtained from EoS is a unique trait of the SAFT implementation used describing the macroscopic properties of the Mie intermolecular potential, allowing for fast and accurate description of the free energy, and thus chemical potentials of the system.

The top down coarse graining technique used to parametrise the force field is effective at producing robust models with transferability and representability, and can be used with confidence to describe transport and adsorption properties.^{200–203} The methane model presented in this work correctly predicts self diffusivities of

supercritical methane at 303 and 333 K at a range of different pressures (Fig 4.12. The accuracy of the EoS in measuring the self-diffusivities of methane justifies the use of the model in measuring transport coefficients of methane in nanopores.

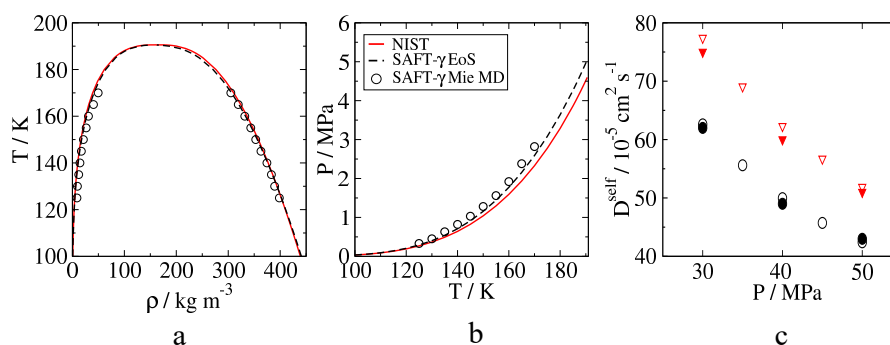


Figure 4.12: Comparison between experimental data and the SAFT- γ EoS and MD simulations describing saturation properties of methane. **a** temperature vs saturated densities, **b** vapour pressures vs temperature. Red line corresponds to smoothed experimental data,²⁰⁴ open symbols are simulations while dashed lines are the results of the equation of state, the latter two employing the same molecular parameters. **c** Self diffusivity of methane predicted using MD simulations in this work (empty symbols) as compared with literature (filled symbols),²⁰⁵ triangles and circles correspond to $T = 303$ K, and $T = 333$ K respectively.

The slit pore is composed of particles explicitly modelled in an FCC lattice, with self-interaction parameters described using an ad-hoc LJ potential, resembling an organic substrate. The height of the pore is 2.6 nm.

The relationship between adsorbed and bulk densities, and Darken factors is seen in Figure 4.13 (Left), where it is seen that at low bulk densities, adsorbed densities are higher than bulk densities. The pore is slightly wider making surface adsorption less pronounced than the adsorption for Case I. Furthermore, relative to the solid particles used in Case I, the solid particles here are larger with a smaller ε , thus leading to weaker attractive energy density, and thus adsorption capacity.

The comparison between the BD-NEMD and EqMD techniques is presented in Figure 4.13 (Right), showing the remarkable agreement between the two methods, with agreements from the dilute limit to very dense fluids spanning orders of magnitude.

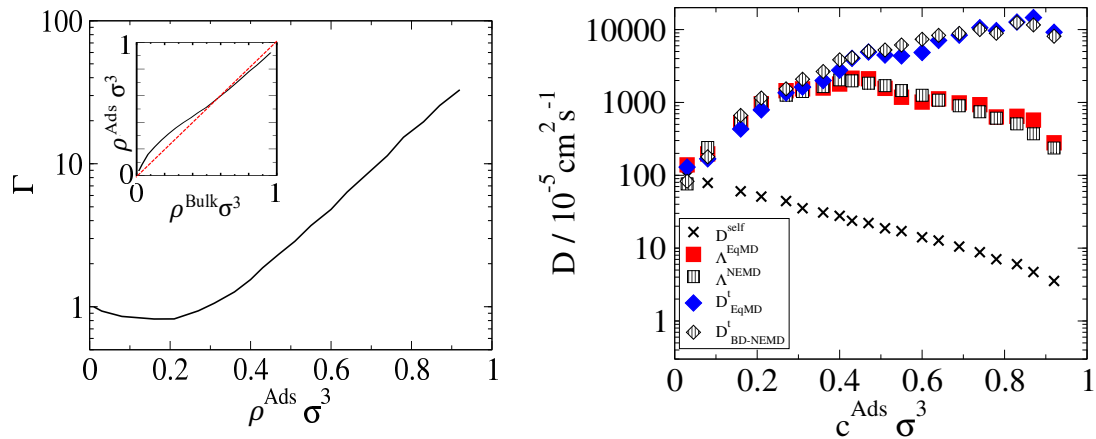


Figure 4.13: *Left* ρ^{Bulk} vs ρ^{Ads} and the Darken factors for methane in 2.6 nm wide slit pore specified in Case II. *Right* Summary of diffusivities of pure methane in the pore in Case II. Squares are the collective diffusivities, and diamonds are transport diffusivities. The striped white symbols are from BD-NEMD simulations and blue and red are measured using EqMD.

4.4.3 Case III: Transport of a Binary Mixture of Two Methane-Like Fluids with Different Adsorption

Case II was extended by introducing an additional fluid component with similar characteristics to the methane model, henceforth described as MA. This new fluid, MB, has the same intermolecular interactions except that its interaction with the solid pore is less favourable. The cross species energy, ε_{ij} , was made 20 % less than the MA-solid interaction (Table 4.1). In the bulk, there is no difference between the two fluids, and the mixture can be seen as having the same bulk properties as pure MA at the same total density. However, the reduction in the value of the cross-species interaction results in slightly different adsorption isotherms, and different pore selectivities.

In order to observe the adsorption behaviour of the binary mixture, pure component adsorption isotherms are evaluated and can be seen in Figure 4.14. Ostensibly, the adsorption isotherms of the pure fluids look very similar, but given the different interactions with the pore, in a binary mixture it is expected that the pore would be more selective toward species MA. IAST is used to correlate the adsorption isotherms of the mixture using the pure component adsorption isotherm, estimating

pore loadings using bulk pressures and compositions.^{187,188} The predictions of the IAST were then validated against EqMD simulations of binary mixtures, results that can be found in Figure 4.15. Generally, higher partial pressure of each species leads to higher adsorption of said species.

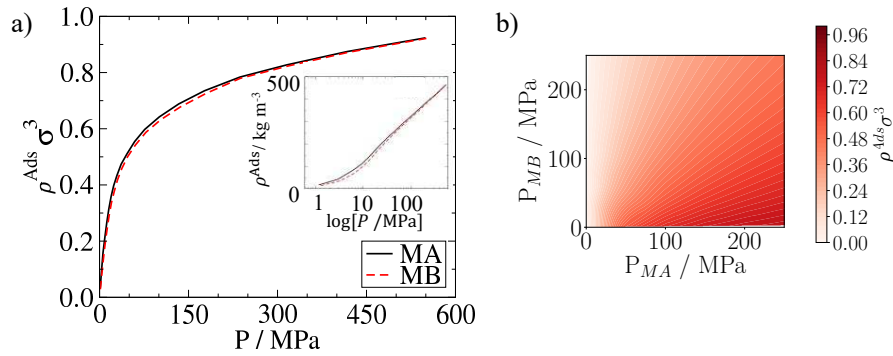


Figure 4.14: *a*: Pure component adsorption isotherms of species MA (solid line) and MB (dashed line) at $T = 298$ K. *b*: Adsorption isotherm for species MA as a function of partial pressures of MA and MB.

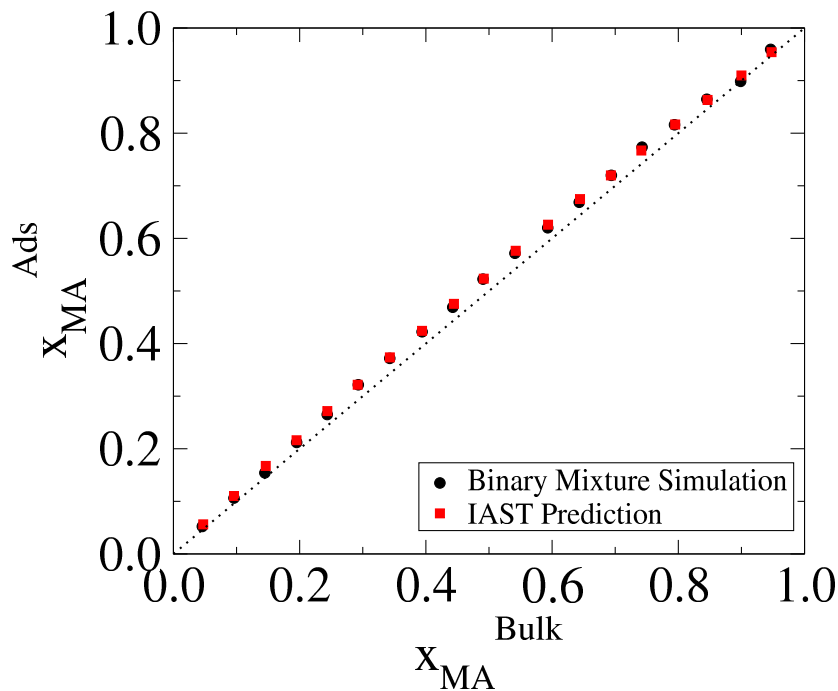


Figure 4.15: Prediction of the adsorption of the binary mixture of studied in Case III at different compositions for a fixed mixture global density, $\sum_i \rho_i \sigma_i^3 = 0.5$, corresponding to a pressure 46 MPa. IAST predicts binary adsorption using pure component adsorption isotherms. Both IAST and binary mixture simulations indicate a slight selectivity towards species MA, which has a higher fluid solid interaction than species MB.

Pore selectivity toward species MA is defined:

$$S_{MA} = \frac{x_{MA}^{Ads} x_{MB}^{Bulk}}{x_{MB}^{Ads} x_{MA}^{Bulk}} \quad (4.4)$$

Where x_i is the mole fraction of species i and the superscripts *Ads* and *Bulk* refer to compositions inside the pore and in bulk. A value greater than one refers to a pore that is more selective towards species MA.

Figure 4.16 (Left) showcases pore selectivity, with selectivities of up to 16 % at the lowest pressures (or bulk densities). With increasing pressure the pore become less selective. The main difference between the adsorption behaviour of the two species is the amount adsorbed nearest to the pore surface, where species MA is adsorbed considerably more strongly than species MB, given the less favourable interaction between species MB and the solid. With increasing densities, the first few monolayers near the pore surface become filled and adsorption occurs in the middle of the pore, which is weakly affected by the solid surface, thus impartially allowing both species to adsorb in the middle resulting in a lower overall selectivity.

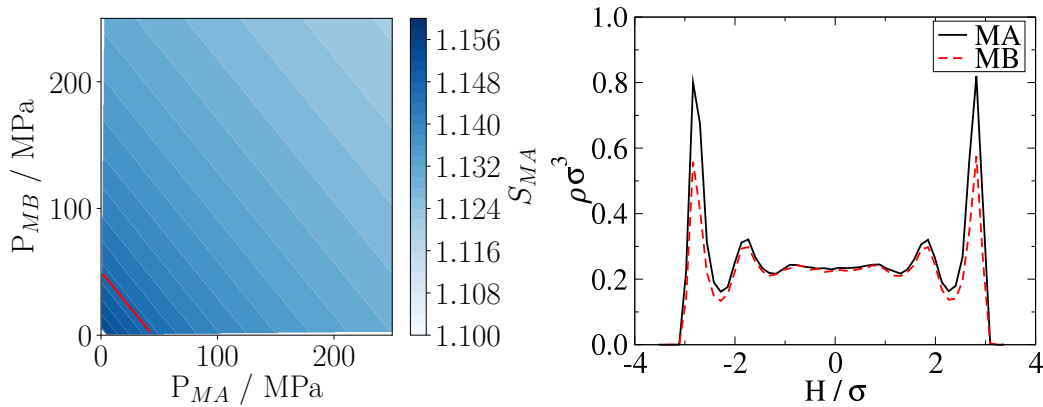


Figure 4.16: *Left* Pore selectivity as a function of partial pressures of MA and MB, with the red line (Equation 4.5) being the region where transport diffusivities have been measured in this work. *Right* Adsorbed densities of MA (solid black line) and MB (dashed red line) measured against pore height, for a system at equilibrium with a bulk equimolar mixture where $\rho_{MA}^{Bulk} \sigma_{MA}^3 = \rho_{MB}^{Bulk} \sigma_{MB}^3 = 0.25$.

The region outlined by the red line in Figure 4.16 (Left) was chosen as the subspace to measure the transport diffusivity matrix of the mixture. This region

follows the following constraint:

$$\rho_{MA} \sigma^3 + \rho_{MB} \sigma^3 = 0.5 \quad (4.5)$$

Where $\sigma = \sigma_{MA} = \sigma_{MB}$.

In this subspace, the total bulk pressure fluctuates between 46.5-48.0 MPa. As the species adsorb differently inside the pore, by keeping the global composition constant, there are different amounts of MA and MB in the bulk at different compositions, leading to slight difference in pressure. The composition, defined using the mole fraction of species *MA*, x_{MA} , is the independent variable. The pore selectivity remains constant independent of fluid composition, having a value of $S_{MA} = 1.145$.

To measure transport diffusivities from EqMD as benchmark cases, Darken factors were calculated using $\partial \ln f / \partial \rho$ as described in Equation 3.35 (Figure 4.17). Generally, the values of the self-species Darken factor, Γ_{ii} increases with increasing concentrations of species *i*. Moreover, Γ_{ii} is much larger than the cross-species Darken factor, Γ_{ij} , indicating that the fugacity of one species is not as strongly correlated with the changes of composition of the other species as it is with changes of compositions of itself. The transport diffusivity matrix is evaluated using both EqMD and BD-NEMD. Note that for the binary mixture, there are four Λ_{ij} and D'_{ij} to be evaluated, with Equation 3.24 used to measure collective diffusivity matrix, $[\Lambda]$ from EqMD (Figure 4.18). The matrix, along with Γ_{ij} , is used to calculate the transport diffusivity matrix, $[D']$ using Equation 3.35. In general, for this particular system, given the identical interactions between all fluid particles independent of species, it is found that $\Lambda_{MA,MA} \approx \Lambda_{MA,MB}$ and $\Lambda_{MB,MB} \approx \Lambda_{MB,MA}$, i.e. the flux of each species is equally influenced by chemical potential gradients of either species. This trend is also true for the transport diffusivities measured, and these can be seen in Figure 4.19, where filled symbols are transport diffusivities measured using BD-NEMD and the empty symbols are those measured from EqMD. The first column describes the self-transport diffusivities, and the second are the cross coefficients, i.e. the

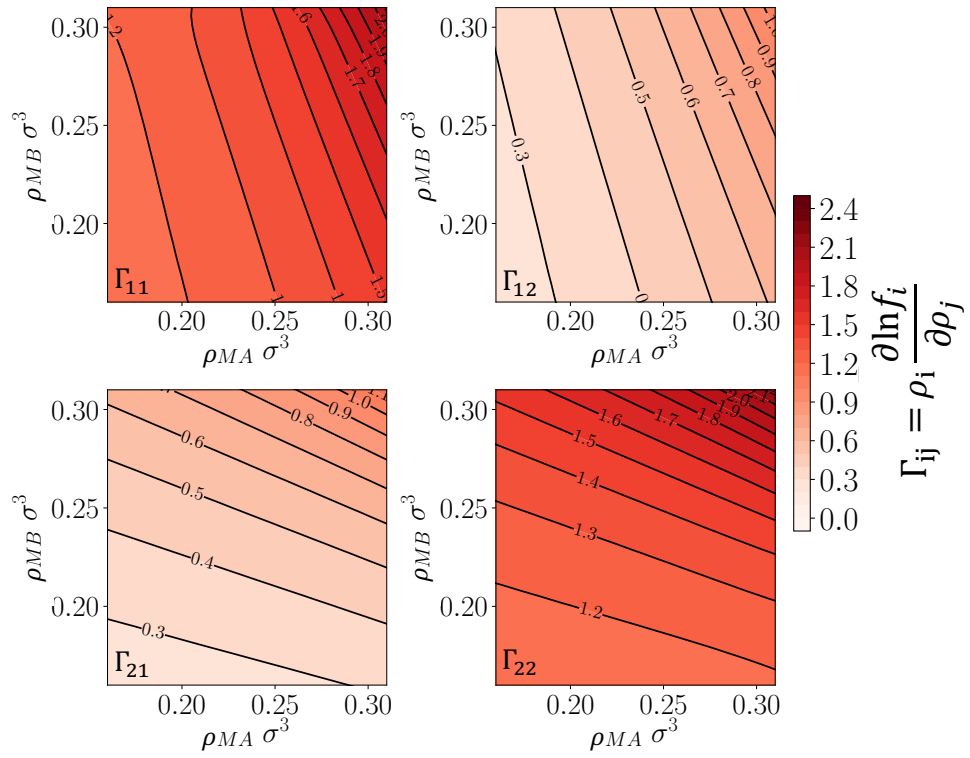


Figure 4.17: Darken Factors of the binary methane-like fluids, where 1 refers to species MA and 2 refers to species MB.

contribution to the flux of species i due to concentrations gradient of species j .

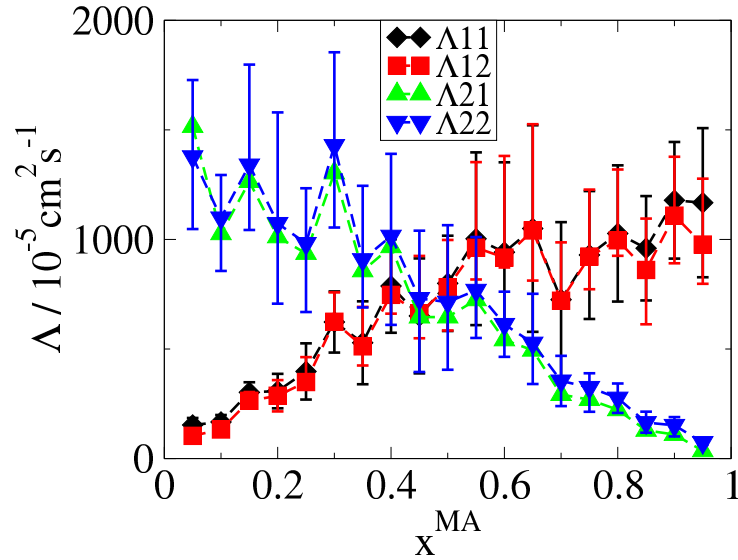


Figure 4.18: Collective diffusivity matrix Λ_{ij} evaluated from EqMD of MA/MB binary mixture at 0.5 total reduced density. Component number 1 and 2 represents MA and MB respectively

D_{ii}^t and D_{ij}^t demonstrate positive linear correlations with molar composition of species i , with the diffusivity of each species approaching zero in the limit of zero concentration. For species MA, in the limit of pure component, i.e. $x_{MA} \rightarrow 1$, $D_{MA, MA}^t$ approaches the value for the pure component system at $\rho\sigma^3 = 0.5$, presented in Figure 4.13. For Case II, $D_{BD-NEMD}^t \approx 3800 \cdot 10^{-5} \text{ cm}^2 \text{ s}^{-1}$ which is in quantitative agreement in the limit of pure component for $D_{MA, MA}^t$. This is not the same for species MB, and the slope describing $D_{MB, MB}^t$ as a function of composition is steeper than that describing $D_{MA, MA}^t$. In the limit of pure component of each species, $D_{MB, MB}^t$ is 10 % larger than $D_{MA, MA}^t$. This does not necessarily mean that species MB travels faster than species MA inside the pore, as a concentration gradient in each species causes significant fluxes in the other species. Nevertheless the high transport coefficients of MB can be explained by lower selectivity of species MB, as MA particles adsorb more strongly to the surface and are slightly slowed down. If we were interested in evaluating transport selectivity, transport diffusivities could be used in continuum models to assess changes in composition downstream of a pore.

Commensurate with previous cases, it is seen that transport diffusivities measured using equilibrium methods have large uncertainties. Moreover, the boundary driven method consistently overestimates the diffusivity, with an average of 18 % for all elements at all compositions. However, the trends are qualitatively consistent with the values measured using BD-NEMD within the uncertainty of EqMD measurements. This deviation is not significant given that values of transport diffusivities span orders of magnitude with changing concentrations, as previously discussed for Cases I and II.

4.4.4 Case IV: Binary Mixture of LJ Fluid with Size Difference

To understand the effect of size heterogeneity on the elements of the transport diffusivity matrix for a binary mixture, the system studied in Case I was modified by adding another species which is 30 % larger than the original LJ fluid, keeping all other self-interaction parameters the same. The pore height is kept the same and the wall particles are thermostated at a temperature of 1.5ε , resulting in a supercritical

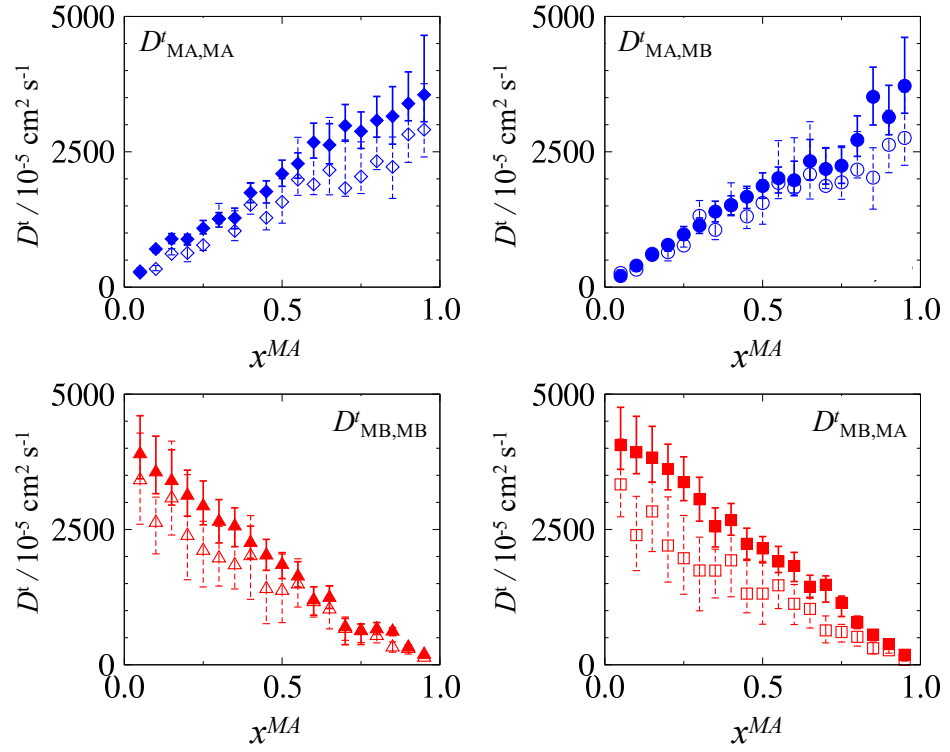


Figure 4.19: Transport diffusivities evaluated for the binary methane-like mixture at total reduced density of $\sum_i \rho_i \sigma_i^3 = 0.5$. Empty symbols are from EqMD, and filled symbols are from BD-NEMD.

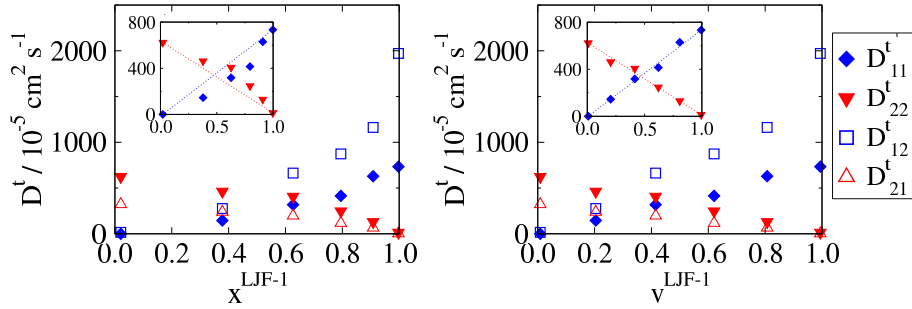


Figure 4.20: Transport diffusivities, D^t , evaluated for Case IV LJ mixture at $\sum_i \rho_i^{Ads} \sigma_i^3 = 0.5$. Here 1 and 2 refer to species LJF-1 and LJF-2 respectively. For this plot, total reduced density was maintained at $\sum_i \rho_i \sigma_i^3 = 0.5$. **Left** Transport diffusivities measured against mole fraction of species $LJF - 1$, x^{LJF-1} , **Right** D^t measured against volume fraction of said species, v^{LJF-1} . The inset plots show the non-linear relationship of D^t_{ii} vs. mole fraction and a linear relationship with volume fraction.

fluid. Henceforth the original LJ species would be referred to LJF-1 and this larger species as LJF-2. From Table 4.1, it can be seen that the cross interaction energy, ε_{ij} ,

between the LJF-2 and LJF-1, and LJF-2 and the solid (LJW) is slightly less than 200 K. This is a consequence of the combining rules used, where the cross interaction energy scales down if the two species have large size differences.

For this system, transport diffusivities were measured for all compositions where $\sum_i \rho_i^{Ads} \sigma_i^3 = 0.2-0.7$. Compared with Case III, there are slight differences in the transport behaviour in this system. To highlight the differences, the concentration constraint used to study Case III, i.e. $\sum_i \rho_i^{Ads} \sigma_i^3 = 0.5$, was also investigated. The results can be seen in Figure 4.20 (Left), where it can be seen that the relationship between transport diffusivity and mole fractions is no longer linear. At intermediate mole fractions, $x^{LJF-1} \approx 0.5$, the self and cross transport diffusivities of species LJF-1 is lower than a linear correlation ($y = x$), and the self and cross transport coefficients of LJF-2 is conversely higher than expected. This is in agreement with previous studies, where strong correlation effects lead to the slow down of more mobile, and less strongly adsorbed species by the less mobile species.²³ Without a linear relationship between mole fractions and transport coefficients, pure component transport diffusivities cannot be used to approximate self-transport coefficients in the binary diffusivity matrix as functions of composition.

Interestingly, a linear relationship becomes apparent when transport is measured against volume fractions, v or by multiplying densities by σ^3 . When volume fraction of species i , v_i , is zero, the self-transport diffusivity of species D_{ii}^t is also zero. The self-transport coefficient linearly increases with increasing volume fractions until the point where v_i approaches 1, when its value approaches the pure component transport diffusivity.

As with previous cases, in this binary mixture, self-transport diffusivities are orders of magnitude larger than self-diffusivities. For the systems presented where reduced density is kept constant, self-diffusivities are independent of composition, having a value of $13 \times 10^{-5} \text{ cm}^2 \text{ s}^{-1}$ for LJF-1 and $10 \times 10^{-5} \text{ cm}^2 \text{ s}^{-1}$ for LJF-2. Again, this is very different to the transport diffusivities seen in Figure 4.20, again emphasizing the fact that self-diffusivities are not adequate parameters to be used in

v_2 %	$D_{1,2}^t/D_{2,2}^t$	$D_{1,1}^t/D_{2,1}^t$	x_1/x_2
20	1.644	1.672	1.682
40	0.622	0.613	0.638
60	0.283	0.282	0.265
80	0.105	0.112	0.095

Table 4.2: The ratio of the elements in each column of the transport diffusivity matrix agree well with the ratio of the molar compositions at different volume fractions at $\sum_i \rho_i^{Ads} \sigma_i^3 = 0.5$. This agreement alludes to the fact that the flow is fully mutualised. 1 and 2 refer to species LJF-1 and LJF-2 respectively.

understanding transport in mesoporous materials.

Moreover, for this system the cross coefficients behave differently to the ones studied in Case III. The cross transport coefficient for each species is not similar to the self term. For species LJF-1, the cross term $D_{LJF-1,LJF-2}^t$ is larger than the self-term, $D_{LJF-1,LJF-1}^t$. For the other species, the opposite trend is observed. As previously described, the mutual diffusivity, D_{ji}^t , quantifies the influence of concentration gradients of species i on the flux of species j . To understand how the concentration gradient of species i affects the flow of both species (i and j), the ratio D_{ii}^t/D_{ji}^t was compared with x_i/x_j at different compositions. If the values of the diffusivity ratio are the same as the composition ratio, it can be concluded that the flow is fully mutualised and there is no transport selectivity. This is because each column of the transport diffusivity matrix describes the resultant fluxes emerging from the same concentration gradient, and if the ratio of the elements of each column of the transport diffusivity matrix ratio is the same as the ratio of molar compositions in the pore, it implies that the fluid is fully mixed, i.e. "toothpaste" or ideal piston flow. One way to confirm mutualisation in slit pores is by observing velocity profiles from external-force (EF-NEMD) simulations,¹⁴⁷ when the force is only applied to one species. This is explored in Figure 4.21 (Left), where it can be seen that by applying forces to all particles of species LJF-2, the velocities of species LJF-1 and LJF -2 are the same, confirming the high correlation between the movement of all molecules. Table 4.2 shows the comparison of ratios and a quantitative agreement is observed.

Although the transport is fully mutualised, composition still affects the overall

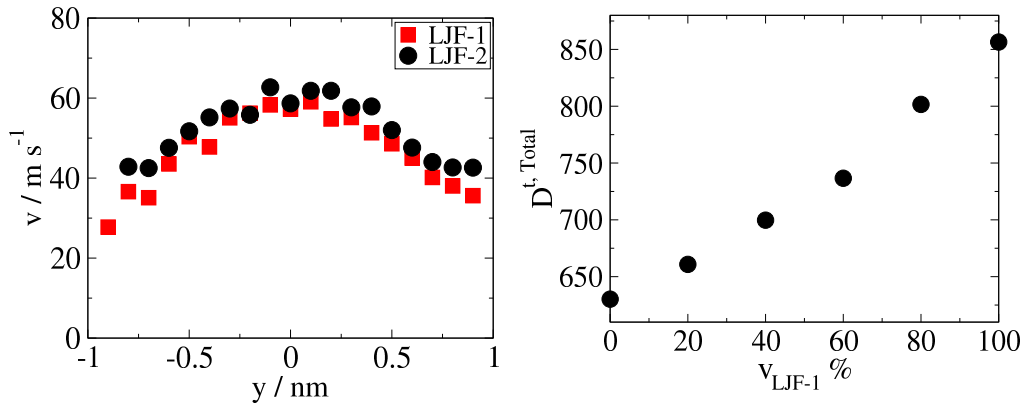


Figure 4.21: *Left* Velocity profiles of species LJF-1 (red squares) and LJF-2 (black circles) when a directional acceleration (0.01 nm ps^{-2}) is applied to all particles of species LJF-2, where $v_{\text{LJF-2}} = 0.4$ and $\sum_i \rho_i^{\text{Ads}} \sigma_i^3 = 0.5$. *Right* Transport diffusivity of the entire fluid, $D^{t, \text{Total}}$ vs fluid volume fraction. Increasing the concentration of the lighter species increases the overall transport of the fluid.

transport. Increasing the composition of the lighter species leads to a faster flow, which can be quantified by measuring the total fluxes and the total density gradient across the pore. The smaller species acts as a diluting agent for the larger species, enhancing overall transport (Figure 4.21 Right).

Back to Figure 4.20, the self transport coefficient of the smaller species is at least 20 % larger than the larger one in the pure component limit, and the cross coefficient of the smaller species is seven times larger. Although these metrics would ostensibly allude to a faster transport of species LJF-1, this is not the correct conclusion, as the fluid is fully mutualised. Yet, it could be seen that for high density fluids inside slit pores, if the adsorption is ideal and the fluid is well mixed, the self-transport diffusivity of each component can be estimated using the linear relationship with respect to the volume fractions. Moreover, if the transport is fully mutualised, the cross terms can be estimated using the ratio of the molar compositions.

The complete picture of transport diffusivity matrix of this system as a function of the adsorbed concentration of both species can be found in Figure 4.22 .

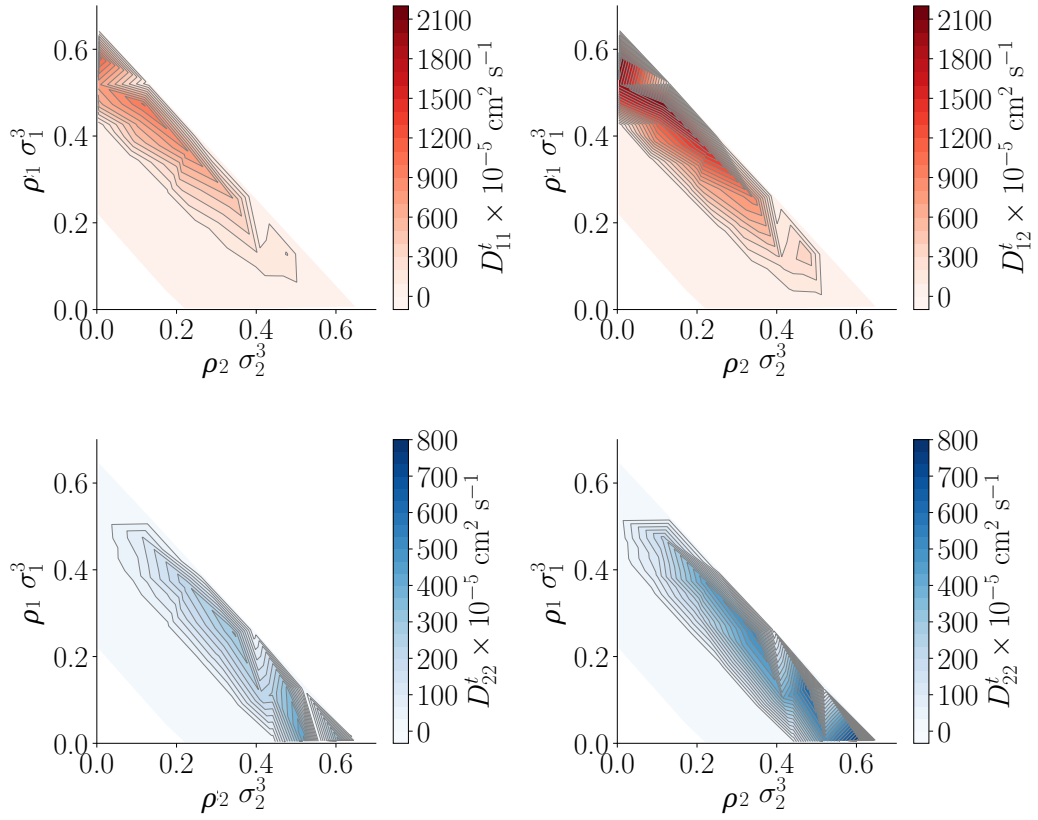


Figure 4.22: Elements of the binary transport diffusivity coefficients of the binary fluid for Case IV. Like previous figures, 1 and 2 refer to species LJF-1 and LJF-2 respectively.

4.5 Conclusions

This chapter validates the assumptions currently used in BD-NEMD methods in measuring transport diffusivity of pure components. By benchmarking values of transport diffusivity obtained using BD-NEMD against those from EqMD, it was highlighted that current implementations of this non-equilibrium method, where it is assumed that concentration gradients can be calculated using bulk reservoir concentrations on either side of the pore, can lead to spurious values of transport diffusivity. By relating bulk concentrations on each side to their adsorbed concentrations at equilibrium, and using adsorbed concentration gradients it was shown that the BD-NEMD can accurately be used to compute transport diffusivities with much lower uncertainty than EqMD methods.

To relate EqMD collective diffusivities to transport diffusivities, Darken correction factors are required. Commonly, these correction factors are assessed using GCMC methods. In this work a novel method was introduced, whereby Darken factors are evaluated for systems where intermolecular interactions are described using Mie potentials. Using the same system used for BD-NEMD at zero force, the equilibrium bulk compositions for each system are used to calculate chemical potentials from the molecular based equation of state, SAFT- γ Mie. A Python code for the evaluation of the SAFT- γ Mie EoS is already available.²⁰⁶

For dense fluids and liquids it is shown that transport coefficients are orders of magnitude larger than self diffusivities. Although there is no formal expectation that these two quantities match except at the ideal gas limit, it is a frequent working assumption which is proven wrong.

In dense binary systems the influence of the adsorption selectivity on transport is minimal, at least for modest differences in pore attraction. The influence of the size of the particles is, on the contrary, more pronounced. Larger particles dominate the transport and it is seen that the transport cross coefficients become relevant. These significant values of cross coefficients result in mutualised flow in slit pores at high densities, i.e. no transport selectivity is observed. It is important to note that these heuristic observations apply solely to smooth pores. Considerable differences arise when examining transport in rugous nanopores, as detailed in the following chapters.

Chapter 5

Significant Effect of Rugosity on Transport of Hydrocarbon Liquids in Carbonaceous Nanopores

5.1 Introduction

This chapter focuses on the dynamics of hydrocarbons confined within models of pores which resemble the relevant pores of shale rock. This has direct implications for fuel production from unconventional reservoirs.

Experimental studies on fluid transport in shale matrix are strongly hampered by the heterogeneity of the samples²⁰⁷ and the inherent barriers to the characterization of nonporous natural rocks at the nanoscale. NMR studies have explored the wettability of oil and water in shale rock, studying pore hopping and resident times of fluids at the surface of the pores.^{208–210} Similarly, diffusion of hydrocarbons through shale-like and kerogen structures have been determined experimentally,^{44,45,211} showing slower pore self-diffusivities relative to bulk systems. Multidimensional CT scans have been

valuable in revealing details of the convective flow in porous media.^{51,212}

As complementary tools to experiments, theoretical and computational techniques have also been used to understand flow of hydrocarbons in organic shales in greater detail. For large domains ($\approx \mu\text{m}$), apparent permeability and pore-network models,^{213,214} lattice Boltzmann simulations,^{215–218} and similar theoretical models^{219–223} have been used to model flow of hydrocarbons in shales. These models are versatile tools that are used to investigate sensitivity of transport to model features, such as slippage, adsorption, pore size distribution, tortuosity, pore geometry and the organic matter content of shales.^{224–226} Conversely, a fine-grained representation of the fluids and solids can be studied using molecular simulations, albeit in smaller domains ($\approx 10\text{ nm}$) and at the expense of larger computational effort. Density profiles inside the pore can give an understanding of heterogeneity inside the pores and velocity profiles can indicate the extent of slip near the walls. Moreover, diffusivities and permeabilities inside pores can be calculated by inducing gradients across the pore. Thus, parameters used in large scale simulations can also be assessed using molecular simulations.

There have been efforts to understand flow in more realistic mesoporous kerogens. Two examples that are of relevance are the model of Sun et al.²²⁷ and the dual-porosity model of Rezlerova et al.²²⁸ These models build the pore surfaces using kerogen molecules. Although this makes the pores more realistic, the surface heterogeneity can make it difficult to decouple different contributions to the flow. These models, do however, suggest that surface roughness has a dramatic effect on the gas flow patterns.^{229,230} Particularly relevant to this manuscript is the report by Wang et al.²³¹ on the adsorption and pressure-driven flow behavior of multicomponent hydrocarbon mixtures through realistic shale kerogen nanopores. A key finding is the demonstration that due to the inclusion of realistic rough surfaces in shale models, hydrocarbons exhibit a parabolic velocity profile in the central pore, while a "sticky" layer forms upon the kerogen surface.

For the transport of dense fluids and liquids in nanoporous materials, there have been much fewer studies than for gases, with early studies focusing on the flow of

hydrocarbons in microporous materials,^{30,232} where a diffusive flow is observed. For mesoporous materials, flow is significantly affected by the type of the solid material, with oils having different slip depending on the nature of the solid. Wang et al. studied the flow of oils in organic²³³ and inorganic²³⁴ slit pores. It was shown that for oils in carbon slit pores, there is fast plug flow transport with large slip lengths. However for inorganic slit pores composed of montmorillonite, parabolic velocity profiles with finite slip lengths were observed. The latter has been supported by other studies investigating flow of oil in inorganic dolomite pores.²³⁵ The difference between flow in organic and inorganic pores has been attributed to the solid fluid interaction, with a strong solid fluid interaction causing a friction on the surface, and a weak attraction leading to plug like behaviour. Other studies that have looked at transport of mixtures of hydrocarbon liquids in mesopores.^{105,236} However, transport selectivity of hydrocarbon mixtures have not been studied for liquid mixtures. In addition, the effect of surface roughness on the flow of hydrocarbon liquids has not been systematically studied.

In this chapter, we measure transport coefficients of binary mixtures of liquid alkanes (n-octane and n-hexadecane) in 3 nm smooth and rugose slit pores using boundary driven non-equilibrium molecular dynamics (BD-NEMD), a method recently extended to mixtures.^{25,237} Although it has been shown that this method is very efficient in measuring transport diffusivities of supercritical fluid mixtures²³⁷ it has not been used to study transport of liquid hydrocarbons. Two classes of rugosity is modelled: ridged and stepped pores. Transport diffusivities and permeabilities are measured for different pores. For the same systems studied, external force NEMD (EF-NEMD)¹⁴⁸ and equilibrium molecular dynamics are also used to independently measure transport coefficients from underlying Onsager coefficients, thus testing the accuracy of the BD-NEMD method. Moreover, EF-NEMD is used to obtain velocity profiles to show the impact of rugosity on slip.

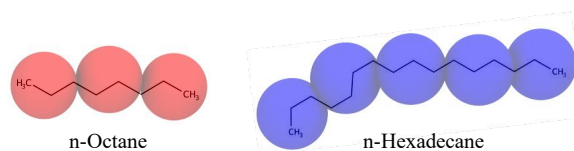


Figure 5.1: Coarse-grained representation of C_8 (*Left*) and C_{16} (*Right*).

5.2 Methodology

5.2.1 Model Definition

We consider a model of a binary liquid hydrocarbon mixture, composed of n-octane (C_8) and n-hexadecane (C_{16}) at typical reservoir conditions of 300 K (80.33 °F) and 300 bar (4351 psi). The nominal pore size is 3 nm. These conditions were chosen as being prototypical of oils in shale.

Force Fields

In this work, we have used a coarse-grained force field based on a mapping to experimental bulk-phase behaviour¹⁹⁹ using the Statistical Association Fluid Theory, SAFT- γ Mie^{130,175} equation of state (EoS). These models share the accuracy of classical atomistic models²³⁸ while neglecting irrelevant levels of molecular detail in order to accelerate the production of results.¹⁷⁶ The coarse-grained (CG) models used to represent n-octane (C_8) and n-hexadecane (C_{16}) are presented in Figure 5.1. Molecules are modelled as tangentially bonded spheres (pearl necklace models), with C_8 and C_{16} being composed of three and five segments respectively.

Intermolecular (non-bonded) interactions are represented by Mie Potentials while intramolecular harmonic bonds are used to take into account the flexibility of the chains. Details of the force field parametrization, tables of parameters and a comparison of the bulk thermodynamic and transport properties with experimental data are provided in Table 5.1.

The intramolecular parameters for alkanes have been reported by Rahman et al.¹⁸¹ and were directly used in this work. These are provided in Table 5.2.

Table 5.1: Self-species intermolecular interaction parameters for the species used in this work.

Molecule	m^{seg}	λ	$\sigma / \text{\AA}$	$\epsilon/k_B / \text{K}$
n-Octane (C ₈)	3	14.30	4.22	314.7
n-Hexadecane (C ₁₆)	5	15.96	4.38	365.0
Carbon (Gr)	–	12	3.40	28.0

Table 5.2: Intramolecular interactions used for all fluids

μ_b / nm	$k_b / \text{kJ mol}^{-1} \text{nm}^{-2}$	$\mu_\theta / ^\circ$	$k_\theta / \text{kJ mol}^{-1} \text{rad}^{-2}$
σ^{inter}	5542	157	19.27

$$\begin{aligned}
 u^{bond}(b) &= \frac{1}{2} k_b (b - \mu_b)^2 \\
 u^{angle}(\theta) &= \frac{1}{2} k_\theta (\theta - \mu_\theta)^2
 \end{aligned}
 \tag{5.1}$$

Where b and θ refer to bond distance and angle between neighbouring atoms respectively. μ is the equilibrium value and k is the harmonic constant.

To predict the thermodynamic properties of the octane and hexadecane CG models of octane and hexadecane are fitted to experimental saturation properties. The robustness of the parameter estimation can be seen in Figure 5.2 where it could be seen that saturation properties can be accurately modelled using Mie parameters fitted to saturation liquid density and vapour pressures. Furthermore, the predictive ability of the CG models with transport properties is presented in Figure 5.3, where self-diffusivities and viscosities are compared with experimental data. Again very good agreement is observed.

5.2.2 Models of Carbon Pores

The solid is modelled explicitly with a carbon graphite structure, the structure of which has been discussed in Chapter 2. No intramolecular potential was used for the graphitic pores, however, in order to thermostat the solid, beads are allowed to fluctuate about their equilibrium positions using a position restraint of a harmonic type, with a harmonic constant of $10,000 \text{ kJ mol}^{-1} \text{nm}^{-2}$.

To study the effect of the rugosity, smooth and rugose structures have been kept as

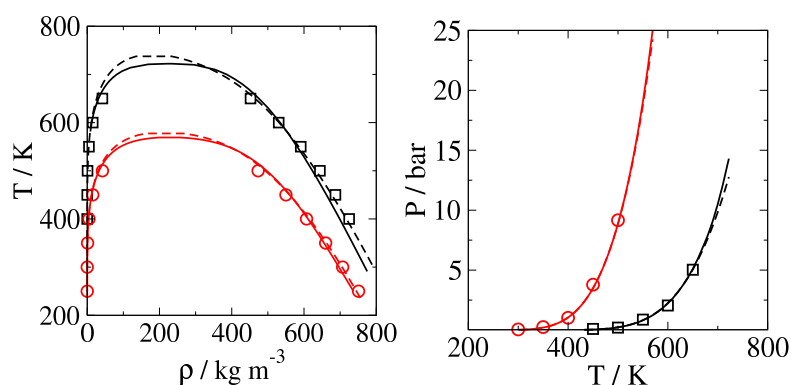


Figure 5.2: Comparison between experimental saturation properties²⁰⁴ (solid curve), with SAFT- γ Mie EoS (dashed curve) and molecular dynamics simulations (symbols). Both molecular dynamics simulations and the EoS use the same parameters. Black squares refer to n-hexadecane, red circles refer to n-octane. **Left** Saturation densities, **Right** Vapour pressures. Error bars within the size of the symbols.

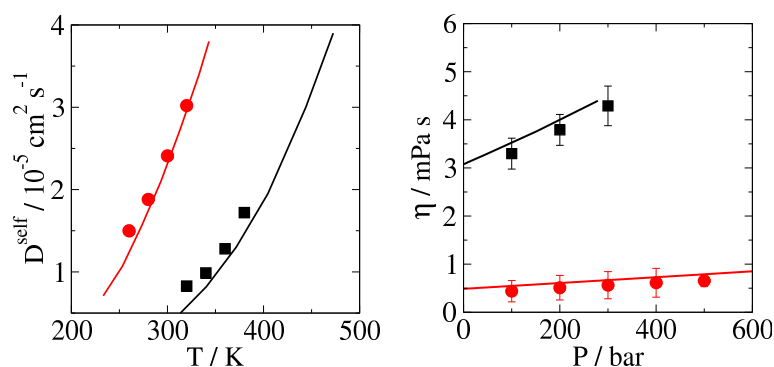


Figure 5.3: **Left** Self-diffusivity of n-hexadecane (black squares) and n-octane (red circles) at $P = 1$ bar. Symbols are simulations and curves are smoothed experimental data.^{239,240} **Right** Dynamic viscosity of the same fluids at $T = 300$ K. Colours and symbols are the same as left, curves are smoothed experimental data.^{241,242}

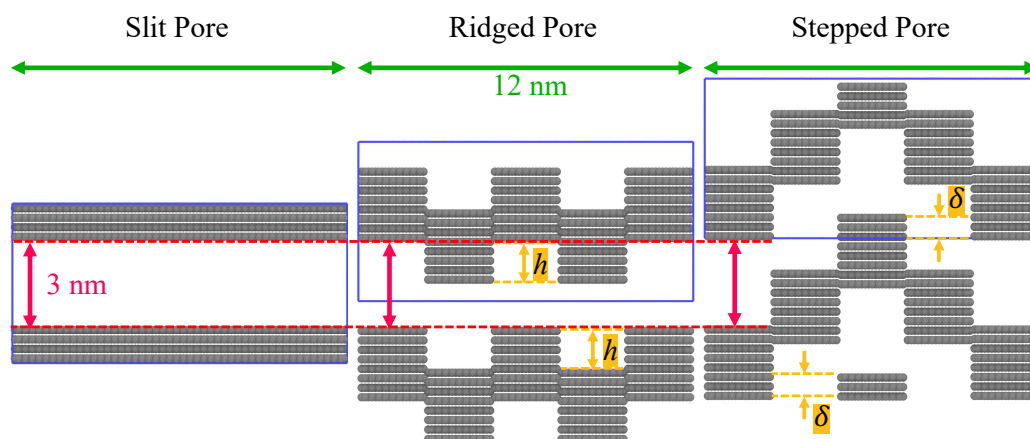


Figure 5.4: The three classes of the carbon pores used to study transport of hydrocarbon liquids. The blue rectangle represents a unit cell, h is the ridge height and δ is the penetration depth. All pores in this study have a pore length (green) of 12 nm and average pore height (red) of 3 nm at any point along the length of the pore. Periodic boundary conditions are applied in the direction in and out of the page

similar as possible, whilst having well defined observables that can distinguish between smooth and rough pores. All pores, rugose and smooth, are designed such that at any point along the length of the pore, the pore height and subsequently the cross sectional area of the pore is the same. To achieve this, pores were modelled explicitly, starting with a block of solid with eight layers of graphite inside a simulation box with a pore length of 12 nm, a depth of 5 nm and a height of 2.72 nm, corresponding to stacking 8 sheets of graphene. The simulation box is set to be periodic. The size of the simulation box is then extended by 3 nm in the direction perpendicular to the plane of the graphite sheets. This results in having a smooth slit pore with a pore height of 3 nm. We note that the definition of pore height is arbitrary and may differ from other, equally arbitrary choices, e.g. the center-to-center distance between the beads of opposing walls. However, the choice made here is governed by the need to define a volume which will lead to the calculation of a pore density which is comparable to the bulk density when the pore is filled. To induce rugosity, the block of solid is further split equally into five smaller blocks and these blocks are shifted up or down to have different structures. These rearrangements can be seen in Figure 5.4.

Ridged pores are similar to smooth pores in that there is an area in the middle of

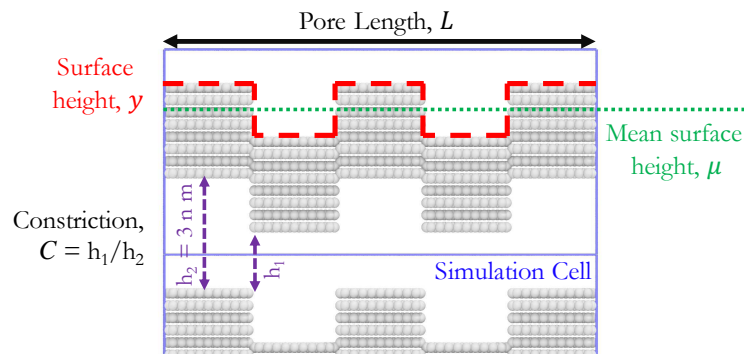


Figure 5.5: Geometrical parameters used to characterise rugosity.

the pore where the flow of the fluid is unhindered and the fluid can stream through the middle. This open path in the middle of the pore becomes smaller as the ridges become more significant. Thus if the ridge height is h , the height of the section where fluids can flow unhindered is $3 - h$ nm. The effect of increasing ridge height on tightening the constriction in the middle of the pore can be seen in Figure 5.5. The effect of ridging is investigated from the smallest of ridges, $h = 0.25$ nm, to relatively large ridges, $h = 2$ nm.

In contrast to ridged pores where there is an unhindered path in the middle of the pore for the liquid to flow, the other class of rugose pores are stepped pores, which are designed such that there is no free path in the middle of the pore as the highest point in the lower wall of the pore is always above the lowest point of the upper wall. This height difference between the highest point of the lowest wall and the lowest point of the upper wall is labelled the degree of penetration, δ . The effect of δ is thus investigated from small values to extreme values.

Pore Characterisation

All pores studied in this work have a nominal height of 3 nm. Pore surfaces are modelled as pristine graphite and thus the only difference between them is from to the arrangement of the blocks. To characterise the arrangement of the blocks, three metrics were used. The first parameter is the ratio between the narrowest and widest constrictions, C (See Figure 5.5).

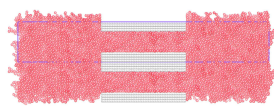
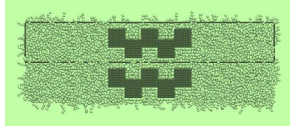
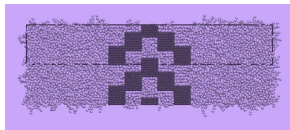
Pore Type		C	R	ϕ	Schematic
Slit		1.00	0.00	1.00	
Ridged	$h = 0.25 \text{ nm}$	0.92	0.08	0.92	
	$h = 0.5 \text{ nm}$	0.83	0.16	0.86	
	$h = 1.0 \text{ nm}$	0.67	0.32	0.75	
	$h = 1.5 \text{ nm}$	0.50	0.48	0.67	
	$h = 2.0 \text{ nm}$	0.33	0.65	0.60	
Stepped	$\delta = 0.0 \text{ nm}$	0.50	0.75	0.67	
	$\delta = 1.0 \text{ nm}$	0.33	1.00	0.60	
	$\delta = 2.0 \text{ nm}$	0.17	1.25	0.55	

Table 5.3: Values of the metrics used to characterise the different pores in this study

The second metric used is the rugosity, R , defined as:

$$R = \frac{1}{L} \sqrt{\frac{\sum_{i=1}^n (x_i - x_{mean})^2}{n}} \quad (5.2)$$

where one sample point is taken at each of the five regions of the solids ($n = 5$) and the different variables are defined in Figure 5.5. A particular advantage of defining R is that stepped and ridged pores can be easily distinguished from each other. The pores are further characterized by the normalised volume-to-surface area ratio inside the pore, ϕ :

$$\phi = \frac{V/A}{(V/A)_{slit}} \quad (5.3)$$

where V is the pore volume, and A is the pore surface area and the subscript *slit* refers to the values for the (pristine) slit pore. Table 5.3 summarises the values of the metrics used in the cases studied.

Adsorption

In molecular simulation studies involving gases, it is typical to determine adsorption as a function of pressures using GCMC. However, for a dense binary liquid mixture under nano-confinement at a pressure of 300 bar, Monte Carlo methods can be less efficient, especially when the liquid is composed of multisegment chains. As a comparison, in this work adsorption behaviour is studied using GCMC and direct EqMD coupled with the SAFT- γ Mie EoS. For GCMC, the Cassandra simulation package²⁴³ is used, a package that is particularly suitable for studying Mie fluids. Configurational bias MC moves are used to aid the insertions and deletions of chain molecules. In each simulation, translation and rotation moves each constituted 35 percent of the moves and insertions and deletions each constituted 15 percent of the moves. Given the high density of the fluid at high pressures, particularly long simulations runs are required. The total number of configurations in each simulation was set to 3×10^9 , with the first 2×10^9 configurations used to equilibrate the system and the remaining used to estimate pressure and adsorbed density.

To verify the robustness of the SAFT- γ Mie EoS in accurately predicting chemical potentials, direct equilibrium molecular dynamics simulation, using the GROMACS/5.1.2¹⁹⁴ simulation package is used. A simulation box is set up with the pore being in contact with two bulk reservoirs on each side of the pore having a similar volume as the porous unit cell, thus increasing the length of the simulation box to 36 nm. To study adsorption, different amounts of both species were randomly inserted into the simulation box, and the simulation was run for 20 ns (using a time-step, Δt , of 2 fs, for 10 million steps). Temperature coupling was applied to both fluids and solid at 300 K using a v-rescale thermostat.²⁴⁴ The bulk density of each species was then used to calculate pressures and chemical potentials using SAFT- γ Mie EoS. Adsorbed densities were also determined as functions of bulk densities. Given that the adsorbed densities and pressures are both functions of the bulk density, they could be easily related.

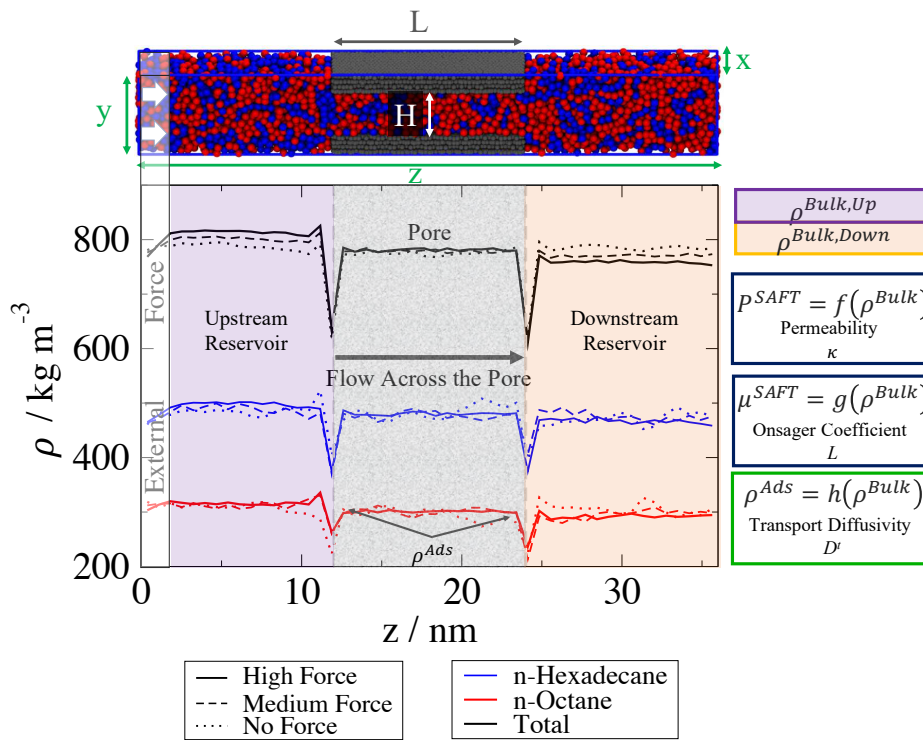


Figure 5.6: (Top) Snapshot from a boundary-driven non-equilibrium molecular dynamics (BD-NEMD) simulation applied to a slit pore. (Bottom) In BD-NEMD an external acceleration (producing an external force) is applied to a small region far from the pore, leading to a density gradient across the pore. Periodic boundary conditions are applied in the z direction which effectively connects the downstream and upstream reservoirs. Note that a larger force leads to a higher density gradient across the pore. (Right) Upon reaching a steady-state, the flux across the pore can be determined. The relationship of the flux to the driving force (the gradient of upstream and downstream bulk densities) allows the calculation of the different transport coefficients. The spike and trough in fluid density near the pore edge are artifacts from density rescaling of the adsorbed fluid.

5.2.3 Boundary Driven Non-Equilibrium MD and Transport Coefficients

A visual representation of the BD-NEMD method is presented in Figure 5.6. For each pore and for each fluid composition, BD-NEMD simulations were run for mixtures of C_8 and C_{16} at $P = 300$ bar using a modified version of GROMACS/5.1.2,¹⁹⁴ which was modified so that accelerations are only applied to the particles in first 2 nm of the length of the simulation cell instead of being applied to all particles. Given that the total length of the simulation box is 36 nm, a 2 nm boundary region was deemed enough to

observe density gradients across the pore. The simulation was run for 20 ns (10 million time-steps using a time-step Δt of 2 fs). The first 4 ns are used for the system to reach a steady state, and the rest of the production was used for analysis.

To minimise the effect of temperature coupling on the dynamics of the fluid particles, temperature coupling was only applied to the solid particles, in addition to applying a positional harmonic restraint to each individual solid particle so that it could only fluctuate about its equilibrium position. For each pore and each composition, 20 independent simulations were run at different applied accelerations, ranging from 0.01 to 0.2 nm ps⁻². All three gradients (density, pressure and chemical potential) were used to assess different transport coefficients.

5.2.4 Darken factor from Neural network

To calculate D^I from Λ (as measured from either EqMD or EF-NEMD), a correction factor commonly called the Darken factor, Γ is required. The Darken factor is related to the slope of the adsorption isotherm.

$$\begin{aligned}\Gamma_{ij} &= \beta \rho_i^{Ads} (\partial \mu_i / \partial \rho_j^{Ads}) \\ D_{ij}^I &= \sum_{k=C_8, C_{16}} \Gamma_{kj} \Lambda_{ik}\end{aligned}\tag{5.4}$$

To evaluate Darken factors, bulk densities in equilibrium were used to calculate chemical potentials using the EoS. Given that there are two species, measuring Darken factors can be quite challenging, as one requires access to partial derivatives of each chemical potential with respect to the adsorbed densities of each species. To overcome this challenge, an artificial neural networks is used to train a model to predict chemical potentials from adsorbed densities. These chemical potentials are calculated using bulk densities of a fluid mixture in equilibrium with the pore, with the adsorbed densities corresponding to the fluid inside the pores. The PyTorch library²⁴⁵ was used for this purpose. Four hidden layers are used in the training of the model, with 32, 16, 8 and 4 nodes in each layer respectively. Exponential linear unit activation functions are used for each node in each layer. Finally, 80 percent of the data are used as the

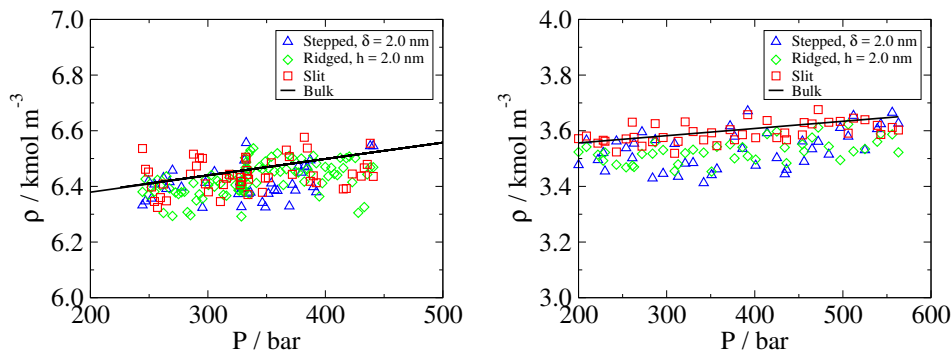


Figure 5.7: Adsorbed densities at different pressures for octane (left) and hexadecane (right) at $T = 300$ K measured using GCMC. Each plot includes results from bulk densities (solid line) and adsorbed densities in three different pores: smooth slit pore (red square) and extremely rugose ridged (green diamond) and stepped pores (blue triangle).

training set and the 20 percent is used as validation. Machine learning is used here as a surrogate for an explicit theory of adsorption. A particular advantage of this method is that partial derivatives of the chemical potential with respect to densities can be measured analytically given the use of automatic differentiation in neural networks.

5.3 Results and Discussions

5.3.1 Adsorption

Adsorption isotherms are determined at different compositions of C_8 and C_{16} for pressures of up to 2000 bar at $T = 300$ K. The relationship between bulk and adsorbed densities can be seen in Figure 5.7. In general the adsorbed density of each species is not significantly different to ρ^{bulk} and the pore is not selective to either species. As a consequence of the high pressures in the bulk region, particles are pushed into the pores and fill all regions of the pores, leading to both bulk and pore regions having very similar densities. Different types of pores, ranging from smooth slit pore to extremely rugose pores, are presented in Figure 5.7, highlighting that rugosity does not seem to play a significant role on the adsorption of the species in the carbon pores. The rugosity considered in this work is not fine-grained. Steps and ridges are

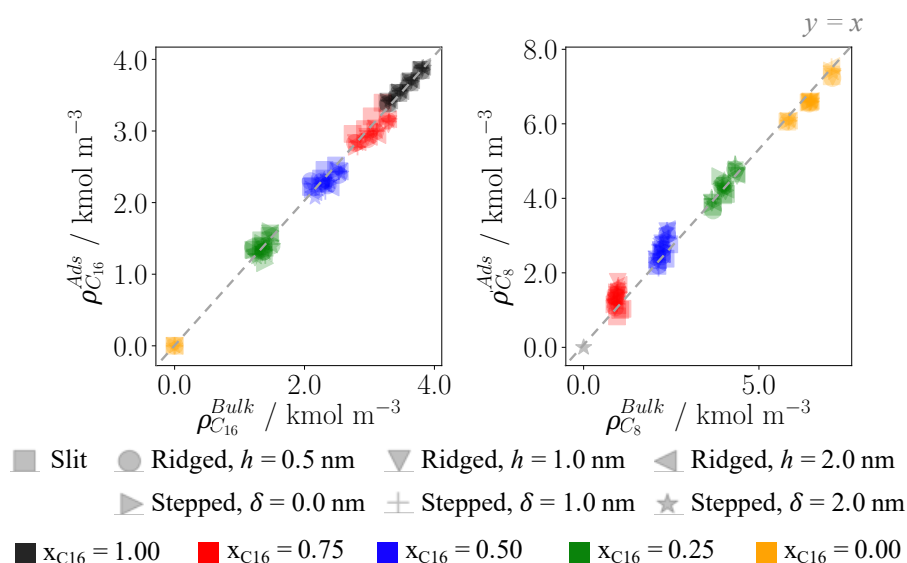


Figure 5.8: Adsorbed vs bulk density for the different pores studied in this work, where each colour represents a different composition. Points with the same symbols and colour represent the system at different pressures. **Left** n-Hexadecane, **Right** n-Octane. There is no apparent adsorption selectivity.

commensurate with the size of the molecules and one would not expect them to geometrically hinder the adsorption of a given component. In a similar fashion, the edges and corners are not expected to selectively change the overall adsorption characteristics of the solid.²⁴⁶ Thus in this work, when using Equation 3.26 to calculate transport diffusivities, it is assumed that bulk and adsorbed densities are equal i.e. $c_i^{Ads} = c_i^{Bulk}$. This is also valid for mixtures, where it could be seen that densities in bulk and in the are the same at all compositions. This can be seen for in Figure 5.8, where for each composition simulations were run at different pressures and the adsorbed density was compared with the bulk composition. No apparent adsorption selectivity is observed across all pores.

Figures 5.9 and 5.10 demonstrates that the rugosity significantly affects the density profile inside the pores. The heat map is generated using bin sizes of $0.5 \text{ \AA}$ and as can be seen more structural ordering is observed with increasing rugosity. However, the peaks of adsorption all have the same order of magnitude, suggesting similar adsorption amount for all systems. Interestingly, the densities presented here are not composition dependent and the mixture is isotropic, suggesting a fully mixed system.

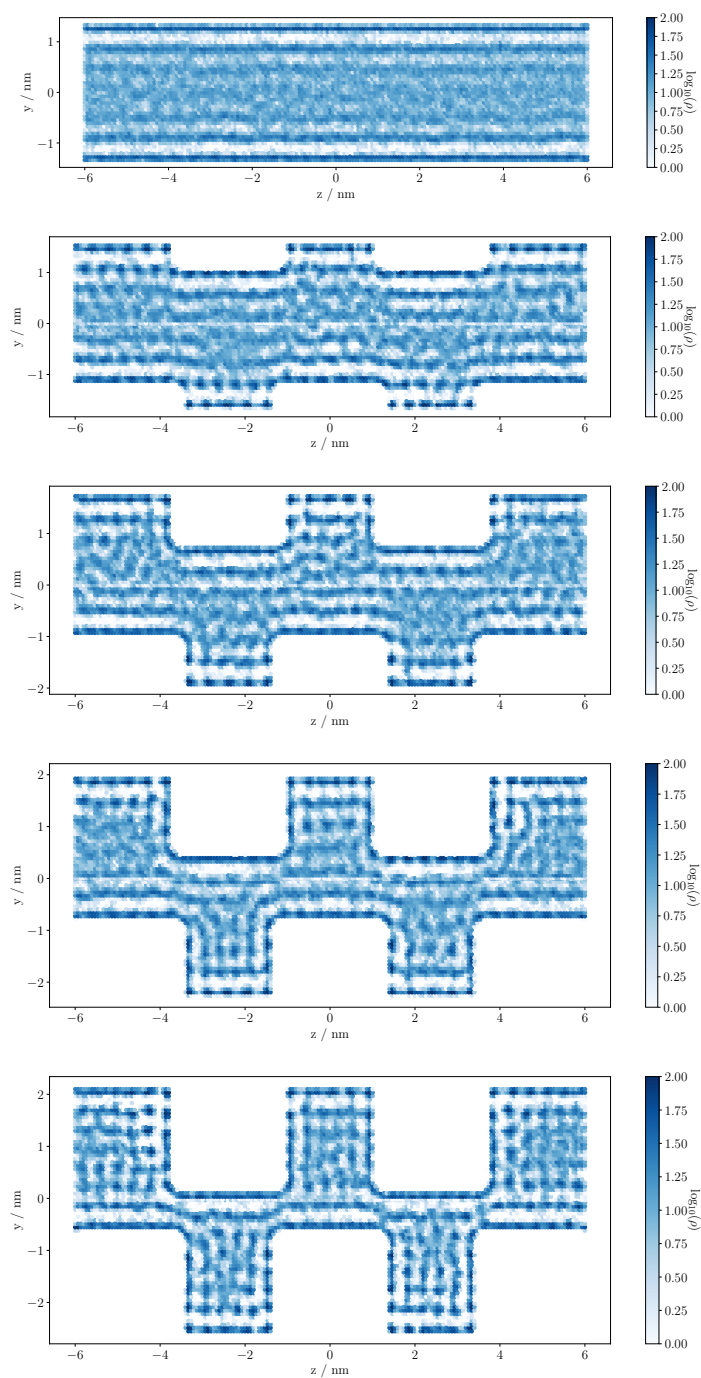


Figure 5.9: Density heat maps of C_{16} (40 mol%) and C_8 measured at 300 K and 300 bar. From *Top to Bottom*: slit pore, ridged pore $h = 0.5$ nm, ridged pore $h = 1.0$ nm, ridged pore $h = 1.5$ nm, and ridged pore $h = 2.0$ nm.

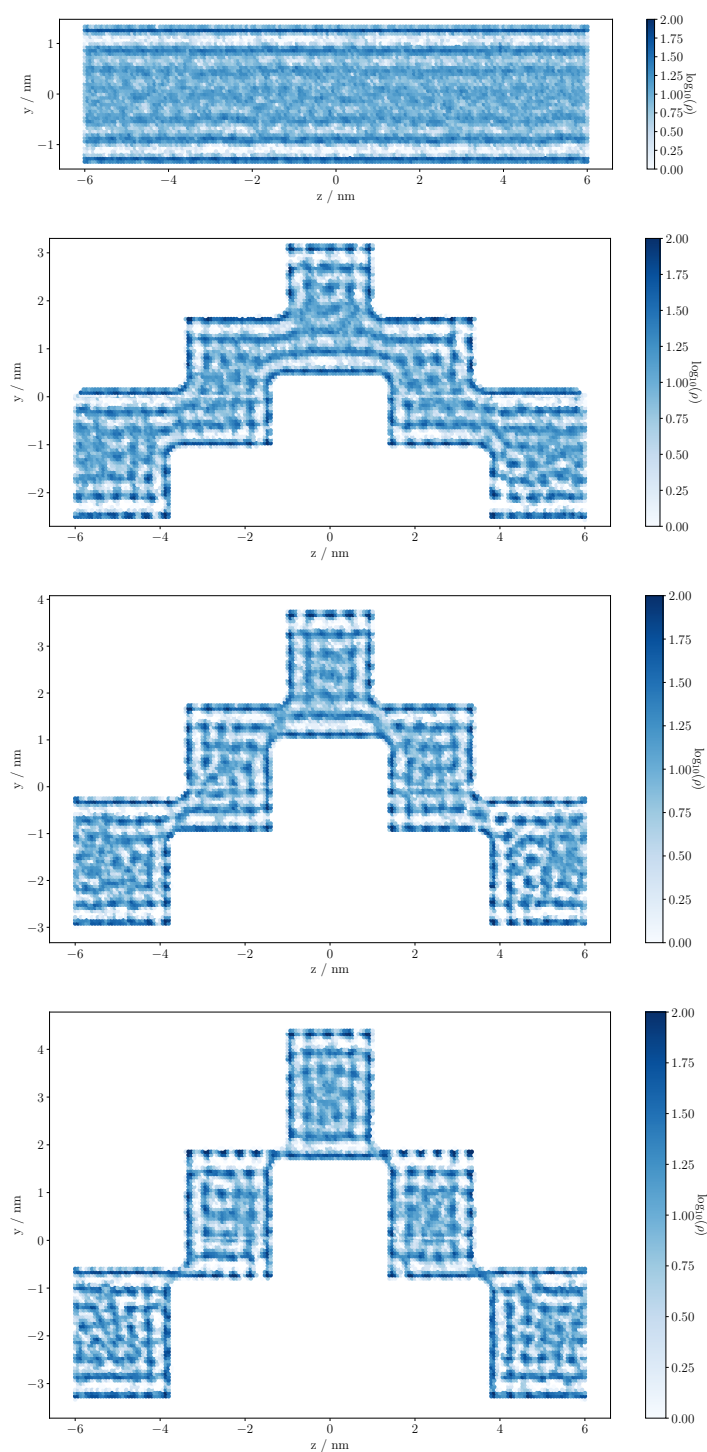


Figure 5.10: Density heat maps of C_{16} (40 mol%) and C_8 measured at 300 K and 300 bar. From *Top* to *Bottom*: slit pore, stepped pore, $\delta = 0$ nm, stepped pore, $\delta = 1$ nm, and stepped pore, $\delta = 2$ nm.

The strong relationships between the chemical potential and the adsorbed densities can be inferred from Figure 5.7 where small changes in adsorbed densities can induce changes in pressures which span hundreds of bars. This is significant in the context of the relating collective diffusivities to transport diffusivities as shown in Equation 5.4. Just like pressures, chemical potentials are extremely sensitive to slight increases in densities, and can increase very rapidly. The link between chemical potential and densities is extremely important in understanding transport, as transport diffusivities can be calculated by multiplying the collective diffusivities by the Darken factor, $\Gamma_{ij} = \beta c_i^{Ads} \partial \mu_i / \partial c_j^{Ads}$. The very high Darken factors seen in these dense liquid systems suggest that collective diffusivities from EqMD cannot be used on their own to interpret transport.

From the above it also assumed that Darken factors can be calculated independent of the pore structure. The result is provided in Figure 5.11 with values in the 100's, making D' two orders of magnitude larger than collective diffusivities. These abnormally high Darken factors are a unique aspect of liquid transport. It is clear from here that for dense confined systems, relying on the use of self-diffusivities or collective diffusivities for describing transport may lead to incorrect conclusions.²⁴⁷

Furthermore, for pure components, $\Gamma_{C_{16}C_{16}}$ is about twice as large as Γ_{C_8,C_8} , as it is less favourable to insert hexadecane particles in a dense hexadecane liquid at 300 bar than it is for octane molecules to be inserted into liquid octane. In general, derivatives of chemical potentials of either species with respect to change in $\rho_{C_{16}}$ are larger than with change in ρ_{C_8} , which is again due to the difficulty of inserting n-hexadecane molecules in a dense liquid phase. Thus Darken factors $\Gamma_{i,C_{16}}$ are larger than Γ_{i,C_8} .

5.3.2 Transport

With BD-NEMD, in order to calculate transport diffusivities, one needs to assess density gradients inside the pore as using the difference between the bulk reservoir densities does not correctly describe motion inside the pores. Figure 5.12 shows the effect of the externally imposed acceleration on the the density gradients inside the

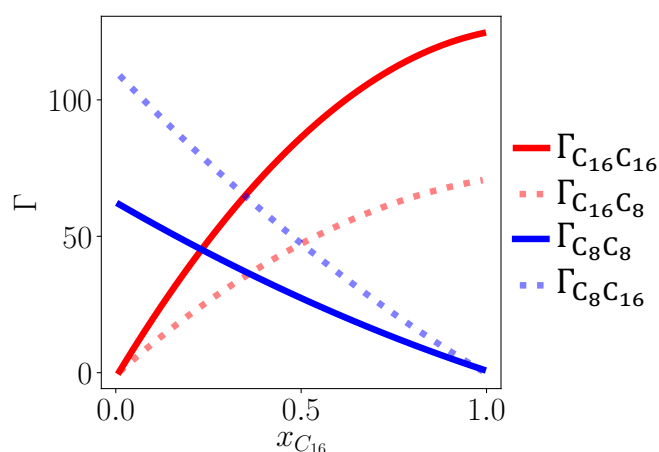


Figure 5.11: Darken factors, Γ , for the binary mixture of C_{16} and C_8 as a function of the mole fraction of the heavier compound $x_{C_{16}}$ at $P = 300$ bar and $T = 300$ K.

pore. As a comparison, a rough pore (stepped pore with $\delta = 0.0$ nm) and the slit pore are presented. As can be seen from the aforementioned figure, applying the external force, creates two reservoir regions with relatively constant densities. The higher the force, the larger the density difference, which then induces a flux within the pore. For the rough pore, the difference in density creates a density gradient within the pore, with densities at the boundary of the bulk reservoir being similar to bulk densities. (Figure 5.12-Left). However, inside the slit pore the density gradient is imperceptible, a result that has been observed for all compositions studied. This flat density cannot be explained from an adsorption point of view, as it could be seen from Figure 5.8 that under equilibrium, increasing densities in the bulk increases densities in the pore. We presume that this unexpected behaviour is a consequence of the extreme smoothness of the slit pores which produces an unimpeded flow, i.e. an unusually fast transport that, in the time/space frame of the simulation, does not allow for the build up of a density gradient in the pore. In the language of friction, these smooth slit pores show an extremely low resistance to flow, a slip condition at the wall, and essentially a rapid plug flow that is not seen when some level of rugosity is applied. Transport diffusivities evaluated using BD-NEMD might not be appropriate to study transport of liquids inside slit carbon pores. The problem can be overcome by

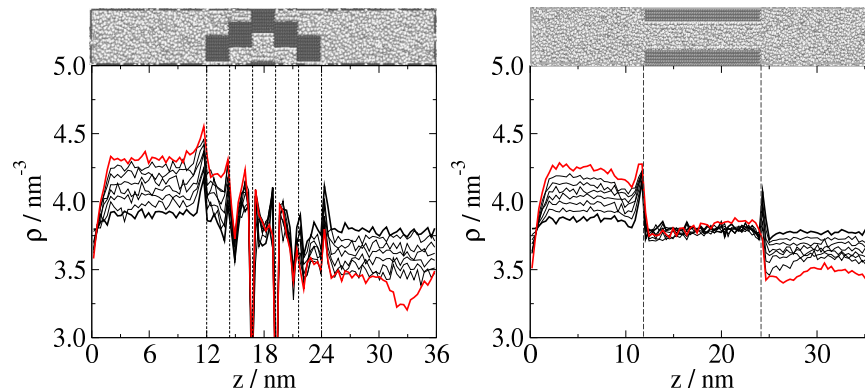


Figure 5.12: Density profiles for pure n-octane for different external boundary forces, thick black line indicates the case with no input force, and thick red line is for the high exerted force. Other black lines are for intermediate forces. **Left** Stepped pore, $\delta = 0$ nm, **Right** Slit pore. Although a clear density profile is observed inside the rugose pore, no density profile is observed inside the slit pore.

using EqMD and EF-NEMD simulations.

In order to compare transport diffusivities between the smooth slit pore and the rugose pores using BD-NEMD, bulk densities were used to measure density gradients across the pores for the case of the slit pore. This leads to a lower bound of the values of the transport diffusivities, but nevertheless allows for comparisons.

Pure Components

Transport diffusivities of pure components within different pores were calculated by relating observed fluxes to density gradients inside the pores. A linear relationship between fluxes and $\partial\rho/\partial z$ is observed for all pores, as presented in Figure 5.13. The log-log plots presented in Figure 5.13c and Figure 5.13d clearly show that a linear relationship is observed independent of the force applied, however a non-linear response of the flux is detected at higher density gradients. By keeping the applied forces within the linear regime (from the point of view on non-equilibrium thermodynamics), we ensure that the induced fluxes are only due to density gradients, and that there are no additional, and spurious, contributions to transport.

To quantify transport coefficients of each component in different pores, the slope of each line is calculated (Figure 5.13). Transport in slit pores is much larger than in

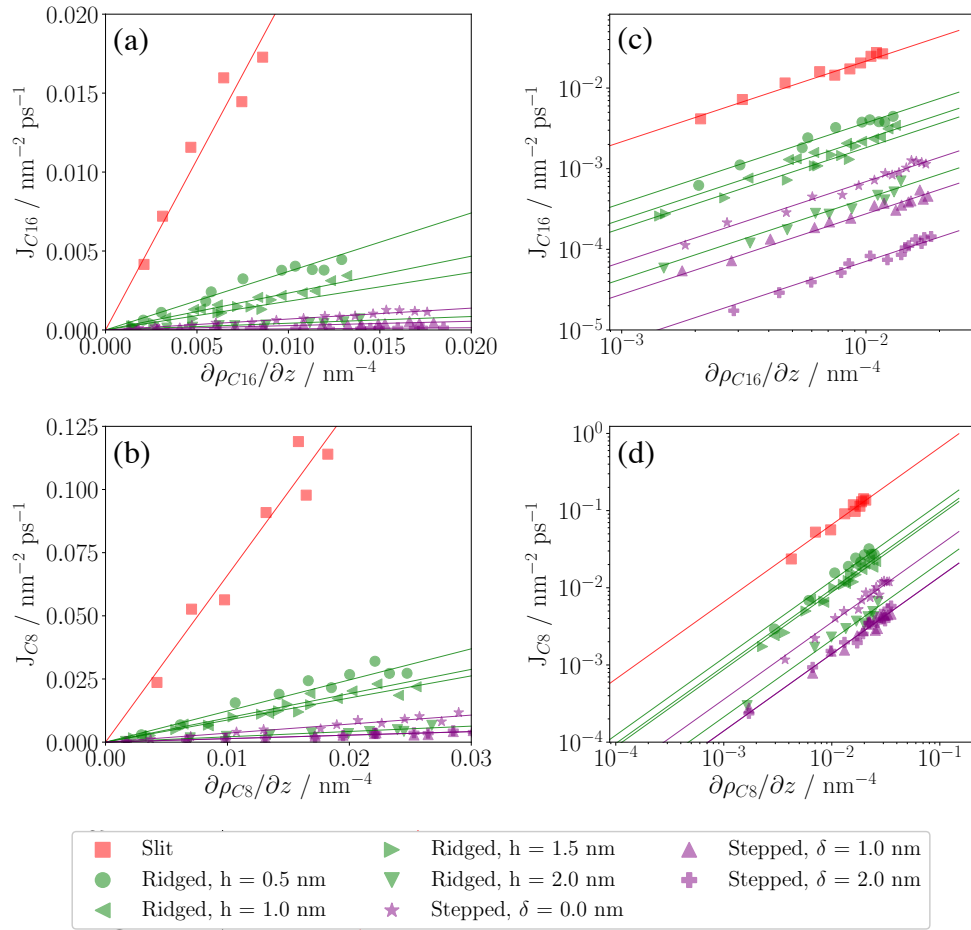


Figure 5.13: Flux, J , vs density gradients, $\partial\rho/\partial z$, for pure C_{16} (**a**, **c**) and pure C_8 (**b**, **d**), in different pores. **c** and **d** are the same as **a** and **b** respectively, using log-log axes instead of linear axes. Symbols are defined in the legend. Red refers to the slit pore, green refers to ridged pores and purple refers to stepped pores.

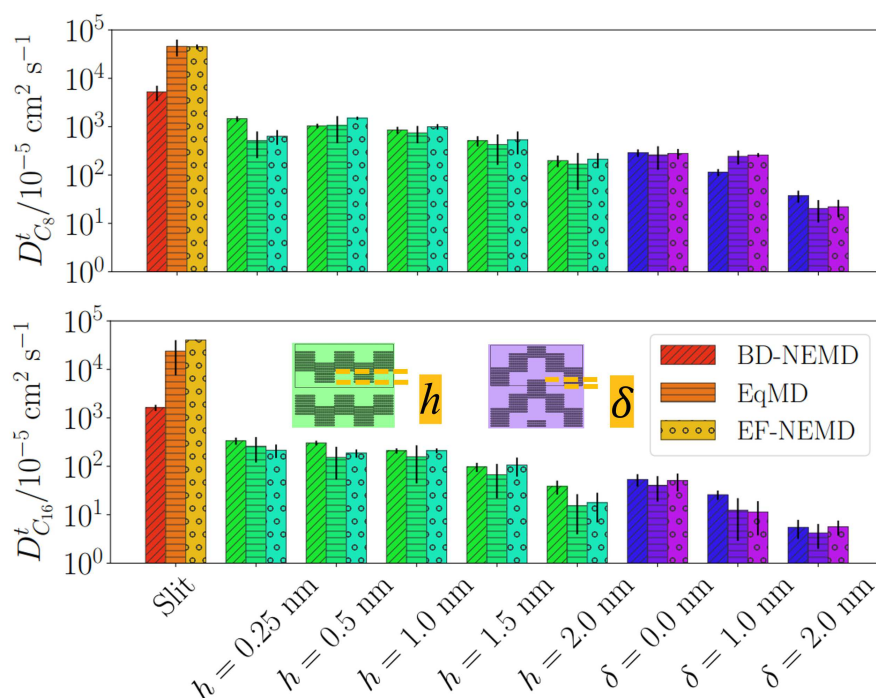


Figure 5.14: Transport diffusivities of pure n-octane (*Top*) and n-hexadecane (*Bottom*) in different pores. For each pore, each transport diffusivity is measured using three different techniques: BD-NEMD (First bar, diagonal hatch), EqMD (second bar, horizontal hatch), EF-NEMD (third bar, circle hatch). Red refers to the slit pore, green corresponds to ridged pores and purple corresponds to stepped pores.

rugose pores. In fact, transport is reduced by three orders of magnitude going from the smoothest (slit) to the least smooth pore (stepped, $\delta = 2 \text{ nm}$). Adding even the smallest of ridge heights, $h = 0.25 \text{ nm}$, leads to an order of magnitude reduction in transport. Interestingly, transport in ridged pores (green symbols) is still much faster than in stepped pores (purple symbols). To investigate why this could be, one has to investigate the relationship between transport coefficients and the different pore characteristics, which is discussed later.

The values of all transport diffusivities for the pure components are summarised in Figure 5.14. In general, transport diffusivity of pure n-octane is much larger than pure n-hexadecane, suggesting faster flow of lighter hydrocarbons in all pores. For the smoothest of the rugose pores, transport of pure octane is three times larger than n-hexadecane, and this ratio increases to 10 for the most rugose pore. Given that for both

species, there is no difference between the adsorbed and bulk densities at 300 bar, this difference between the transport is assumed to not be a consequence of adsorption, but more due to pore geometry and fluid properties. C_{16} becomes slower with increasing rugosity given its larger size.

Values of D^t were also independently evaluated using EqMD and EF-NEMD, and presented in Figure 5.14. For the rugose pores, all methods return similar values of D^t . In EF-NEMD and EqMD, the pore is not in contact with a bulk and essentially flow is measured in an infinite pore. Thus the nature of these simulations is not the same as BD-NEMD simulations. The agreement between the methods for rugose pores suggests the robustness of the assumptions made. Moreover, it suggests that transport is not a function of system sizes or pore lengths in BD-NEMD simulations. However, for slit pores, there is a large discrepancy in the values of the D^t as measured using these different techniques. Particularly for C_{16} , $D^{t,EF-NEMD}$ is 7 times larger than $D^{t,BD-NEMD}$. It could be seen that EqMD and EF-NEMD produce values of transport diffusivity that are larger than BD-NEMD, which is presumed to be a consequence of using bulk density gradients which provide the lower bound of D^t as bulk density gradients are much larger than adsorbed density gradient. As other methods suggest, the reason for this lack of density gradient is that transport is so large that observing measurable fluxes requires extremely small density gradients, which challenges the BD-NEMD method.

Using different techniques has the benefit of being able to evaluate different diffusivities for the same system. The comparison between the values of transport, collective (Maxwell-Stefan for pure components), and self diffusivities is presented in Figure 5.15. Collective diffusivities were calculated from EF-NEMD, transport diffusivities are from BD-NEMD, and self-diffusivities were evaluated using EqMD simulations. As can be seen, increasing rugosity decreases the value of all transport coefficients, and in general, flow is slower in stepped pores than in ridged pores.

A significant result emerges that unlike the flow of gases in microporous materials, where collective diffusivities are assumed to be in the same order of magnitude as self-diffusivities, for dense liquids this is not the case with differences ranging from being

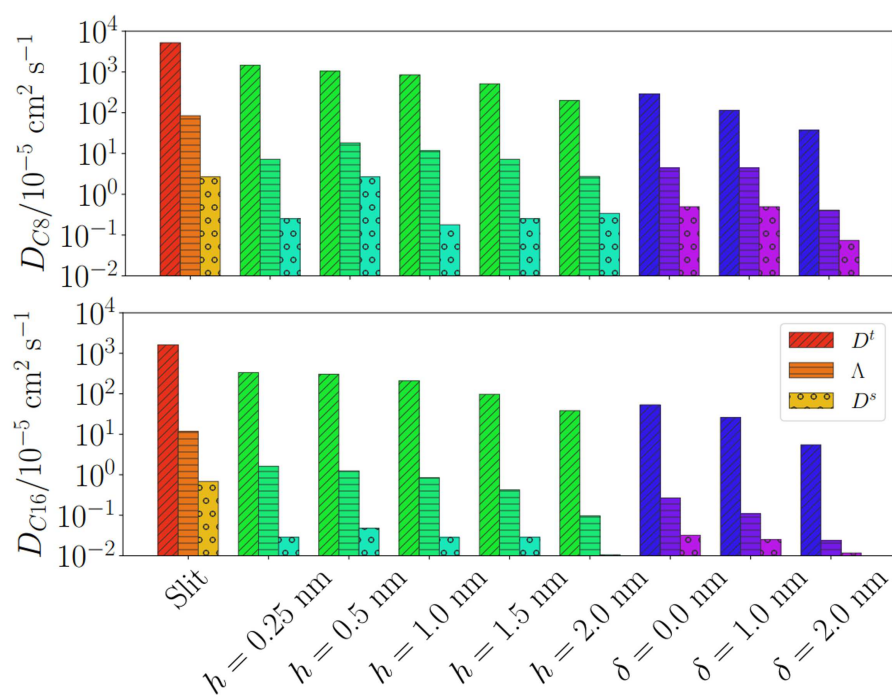


Figure 5.15: Comparison between different diffusivities of pure n-octane (*Top*) and n-hexadecane (*Bottom*) in different pores. For each pore, the first bar (diagonal hatch) corresponds to transport diffusivity, the second bar (horizontal hatch) refers to collective diffusivity, and the last bar (circle hatch) is the self-diffusivity. Red refers to the slit pore, green corresponds to ridged pores and purple corresponds to stepped pores.

almost 30 times larger for the least rugose pores, to around 5 times larger for the most rugose. Increasing roughness reduces the collective motion of particles, thus reducing the ratio between collective and self-diffusivities. Nevertheless, for liquids adsorbed in mesoporous carbon pores at 300 bar, there is a high correlation between the motion of particles and thus one must be careful in using self-diffusivities to describe transport of liquids. Furthermore, self-diffusivities can be an order of magnitude smaller than collective diffusivities, which themselves may be several orders of magnitude smaller than transport diffusivities, given the large values of the Darken factors (Figure 5.11).

The observed transport diffusivities were correlated against the metrics (C , ϕ and R) used to characterise the pores, as defined in Figure 5.5 and Equations 5.2 and 5.3. Naturally, it is expected that having a wide constriction and a large volume to surface ratio would be favourable to transport, i.e. $D^t \propto C$ and $D^t \propto \phi$. Conversely, increasing roughness would hinder transport, i.e. $D^t \propto 1/R$. By plotting D^t against $C\phi/R$, henceforth called the rugosity ratio, two linear regimes were obtained as can be seen in Figure 5.16. For all stepped pores and ridged pores where $h \geq 1$ nm, there is a linear relationship between transport diffusivity and the ratio $C\phi/R$. For less rugose ridged pores ($h \leq 1$ nm), the slope of this relationship changes. This suggests a significant difference in the transport mechanisms and in the influence of rugosity on these. For the more "open" pores, the rugosity only affects the transport close to the surfaces, which are effectively only a small fraction of the pore volume. For tighter pores, changes in rugosity pronouncely affect the flow, as seen in the inset of Figure 5.16.

Importantly, given that the relationship between D^t and $C\phi/R$ collapses onto the same line independent of pore type (ridged or stepped), it could be concluded that the shape of the pore itself does not influence transport, rather it is the intrinsic rugosity of the pore that influences it.

Transport Selectivity in Dense Mixtures

To investigate the effect of rugosity on the transport selectivity of mixtures, velocity profiles were obtained from EF-NEMD simulations using accelerations of 0.4 nm ps^{-2} .

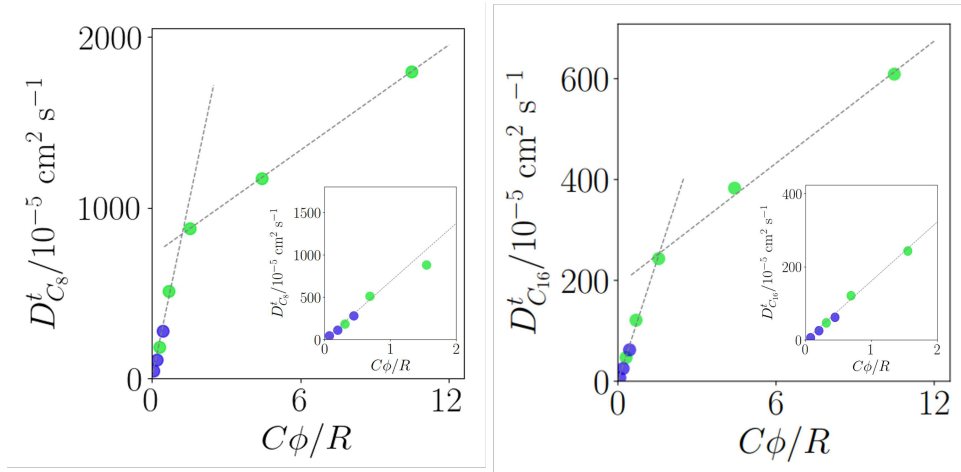


Figure 5.16: D^t vs the rugosity ratio, $C\phi/R$ for C_8 **Left** and C_{16} **Right** in ridged (green) and stepped (purple) pores, indicating two linear regimes. Inset zooms in on the origin.

An important feature of EF-NEMD simulations is that directional accelerations are only applied to one species, yet the velocities of both species can be measured. This provides a qualitative understanding of the degree of mutualisation. If velocities of both species are the same when only one species experiences a force, it could be assumed that the transport is mutualised and there is limited transport selectivity, i.e. the ratio of fluxes of the two species can be assumed to be the same as the ratio of their corresponding mole fractions at equilibrium. In a binary mixture, for the ratio of fluxes to be the same as the ratio of mole fractions, the following relationship must be satisfied:²³⁷

$$\frac{x_1}{x_2} = \frac{D^t_{1,1}}{D^t_{2,1}} = \frac{D^t_{1,2}}{D^t_{2,2}} \quad (5.5)$$

where $D^t_{i,j}$ is the element of the transport diffusivity matrix defined in Equation 3.27, and x_i is the mole fraction of species i . Even for the case where $D^t_{1,1}$ is very different to $D^t_{2,2}$, the cross (off-diagonal) coefficients of the diffusivity matrix can induce mutualisation. A common approach in modelling transport of binary mixtures is to relate the flux of each species to its own density gradient, yet as has been shown here, in the case of dense liquids, it is very important to account for the cross coefficients, as they can significantly affect the interpretation of transport in mixtures.

Figure 5.17 shows two dimensional velocity heat maps of C_8 in a binary mixture of

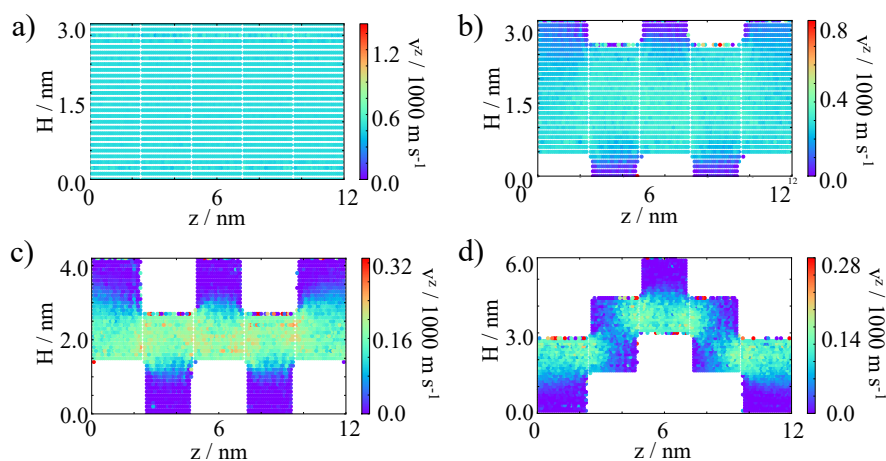


Figure 5.17: Heat maps of velocity, v^z , of C_8 in a mixture of C_8 (60 mol%) and C_{16} in different pores. An external force, with $\alpha^z = 0.4 \text{ nm ps}^{-2}$, is applied only to C_{16} CG segments, leading to a build up of velocity. **a** slit pore, **b** ridged pore, $h = 0.5 \text{ nm}$, **c** ridged pore, $h = 1.5 \text{ nm}$, **d** stepped pore, $\delta = 1.0 \text{ nm}$. Different plots have different color bars.

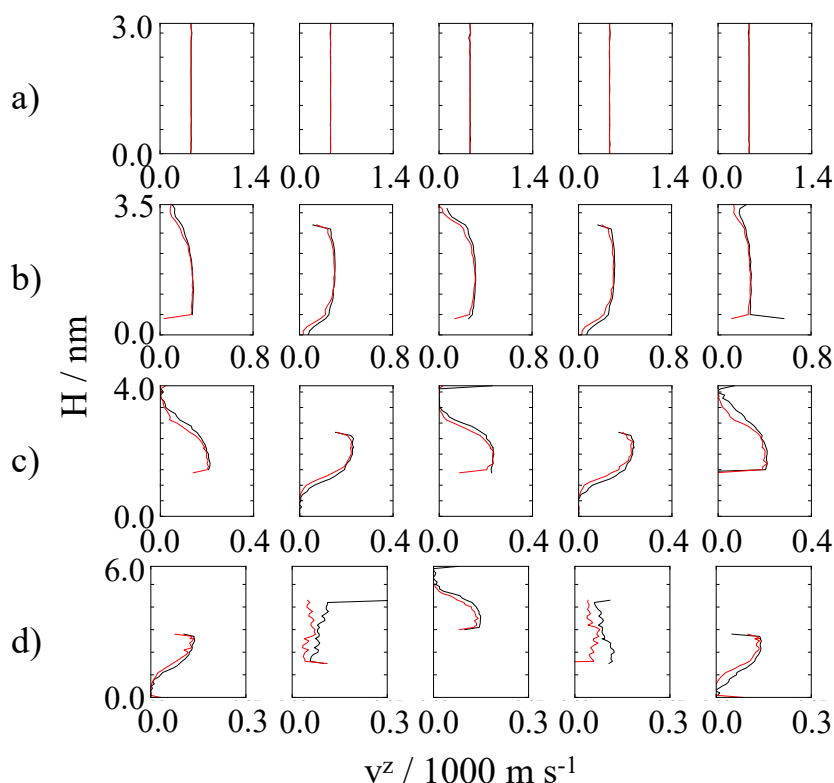


Figure 5.18: Velocity profiles of C_{16} (40 mol%) (black curve) and C_8 (red curve) measured in the middle of each of the five blocks of the pores presented in the velocity heat maps. **a** slit pore, **b** ridged pore, $h = 0.5 \text{ nm}$, **c** ridged pore, $h = 1.5 \text{ nm}$, **d** stepped pore, $\delta = 1.0 \text{ nm}$. Only species C_{16} experiences the external force. Increasing rugosity reduces slip and the plug flow velocity profile is altered. Forces are only applied to C_{16} .

C_8 (60 mol%) and C_{16} in four different pores. In the slit pore (Figure 5.17a), a plug flow is observed where the fluid velocity is constant everywhere inside the pore. This is in agreement with other studies^{39, 40, 56, 233} and highlights the fact that transport is extremely fast given the smoothness of the pore surface. For slightly ridged pores (Figure 5.17b), it could be seen that there are "wells" near the pore surface where the fluid velocity is much smaller than the middle of the pore. Yet these regions are quite small and the fluid velocity in the middle of the pore remains homogeneous.

The effect of rugosity on transport becomes more apparent for the two extreme cases in Figures 5.17c and 5.17d. Particularly obvious for the stepped pore in Figure 5.17d, there are clear regions of high velocity at the boundary between two blocks, while the velocity in the middle of block is small, demonstrating a "hopping" mechanism of transport. This is also observed in Figure 5.17c, where at the boundaries of two neighboring blocks, local velocities are slightly larger. The wells in this pore are very deep. Only near the top of the wells, there exists a measurable velocity. Increasing rugosity leads to large regions of stagnant fluid inside the pores.

The qualitative nature of velocity profiles shown for this composition is the same as observed for other compositions, including the pure component systems. The difference between slightly and extremely rugose pores explains the different regimes of transport as alluded to in Figure 5.16. Clearly, in less rugose pores, the middle of the pore is not strongly affected by the pore surface. However, increasing rugosity results in the stagnation of the fluid inside the wells, which plays a significant role in the overall flow and changes the mechanism of transport. These stagnant regions effectively reduce velocities in the wells to zero, and the reduction in flow velocity propagates to the middle of the pore, changing the velocity profile of the fluid.⁴²

Another key observation emerging from the velocity profiles is that even though the external force only acts on species C_{16} , both species have the same velocities and velocity profiles (Figure 5.18). In essence, hexadecane drags octane along with it, forcing the octane to have the same velocity. Thus, transport of hydrocarbon liquids in carbon pores is fully mutualised, and no apparent transport selectivity is observed in any of the pores.

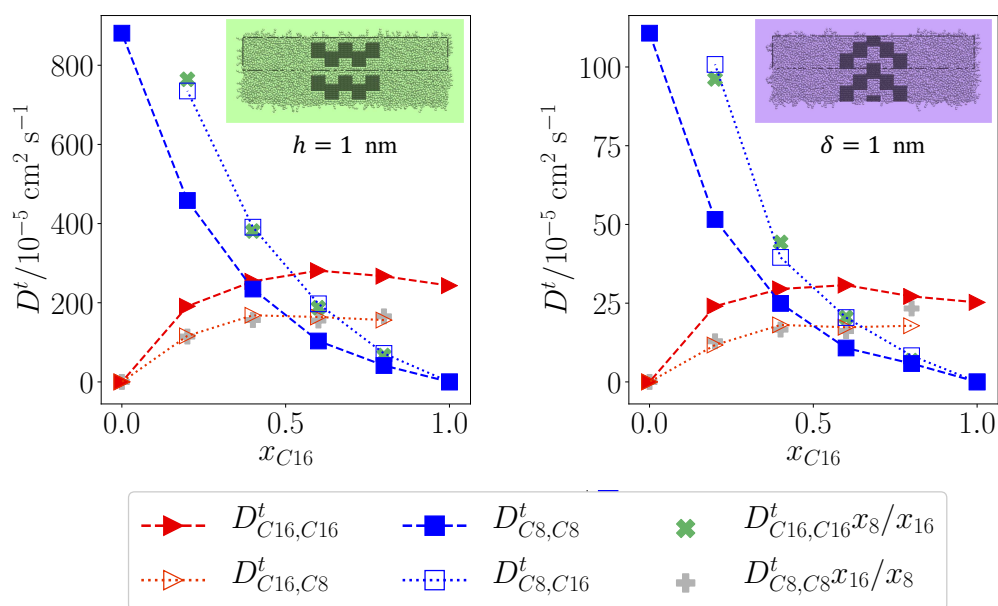


Figure 5.19: Transport diffusivities as a function of concentration for (Left) 1 nm ridged pore (Right) 1 nm stepped pore. Independent of pore type, cross transport diffusivities can be predicted (crosses and pluses) using self-transport diffusivities and adsorbed mole fractions, indicating a fully mutualized flow.

For pure components, it has been shown in Figure 5.14 that transport of pure C_8 is about 4 times faster than pure C_{16} . However, for mixtures, although this still holds for the self-transport diffusivities, i.e. $D_{C8,C8}^t > D_{C16,C16}^t$, the mutualisation is manifested through the cross coefficients of the transport diffusivity matrix. The off-diagonal elements of the matrix describe the extent to which concentration gradients of each species induces flow of the other. This can be seen in Figure 5.19, where elements of the diffusivity matrix are presented for two rugose pores using Equation 3.37. With the assumption that the transport is fully mutualised, the cross diffusivities were also predicted using Equation 5.5, using the self transport diffusivities and the mole fractions of the species inside the pores. It could be seen that cross coefficients can be predicted assuming mutualization.

Even though the fluids are mutualised, the overall transport of the mixture changes with composition. The total flux is fastest when the mixture is composed of pure C_8 , and is reduced with increasing mole fractions of n-hexadecane. Thus, flow of n-octane is slowed down by the presence of n-hexadecane, and transport of n-hexadecane is

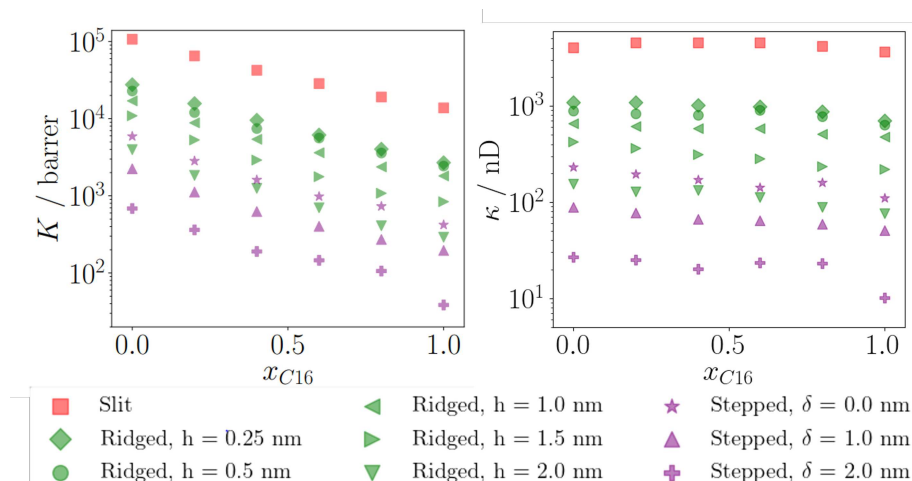


Figure 5.20: *Left* Permeance, K , and *Right* Permeability, κ , vs mole fraction of hexadecane x_{C16} in different pores. 1 barrer = 3.3510^{-16} mol m / m² s Pa and 1 nD = 9.869 cm².

enhanced by the presence of the n-octane. This is in agreement with previous studies of gases, where strong correlation effects slows down more mobile species.²³

To quantify the effect of composition on transport, permeances, K , of all fluids at different compositions within different pores were calculated and can be seen in Figure 5.20 (*Left*). For all geometries, increasing the mole fraction of n-hexadecane in the fluid slows transport exponentially.

For transport of n-alkanes in kerogens, permeability is seen to be a function of fluid compositions. The pores studied here conform in a general way with Darcy's law, with permeabilities slightly changing with composition (Figure 5.20 *Right*). Significantly, it is seen that permeability in the least rugose pores is unexpectedly high (in the order of μDa) whereas values typical for shales are in the order of nD.⁵¹ Increasing the roughness of the mesopores significantly reduces the permeability, with stepped pores having permeabilities of ≈ 10 nD. This clearly highlights the inadequacy of slit pores as models for realistically capturing the transport of liquid hydrocarbons in mesoporous organic shales. One can also calculate the permeance and permeability starting from the collective diffusivity (obtained from EF-NEMD), appropriately multiplied by the Darken factor and converted in accordance to Equation 3.38. The results are consistent with the results plotted in Figure 5.20 and are

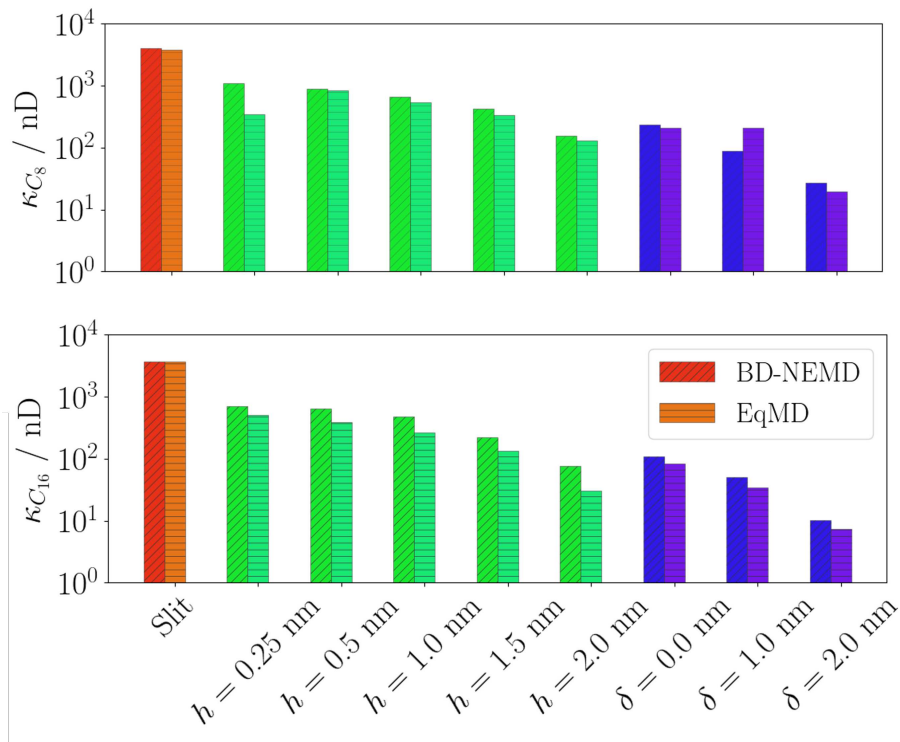


Figure 5.21: Comparison between the permeability of pure n-octane (*Top*) and n-hexadecane (*Bottom*) calculated from two different routes in different pores. For each pore, the first bar (diagonal hatch) corresponds to permeability calculated using BD-NEMD, the second bar (horizontal hatch) refers to that using collective diffusivity. Red refers to the slit pore, green corresponds to ridged pores and purple corresponds to stepped pores.

presented in detail in Figure 5.21.

5.4 Conclusions

The aim of this chapter is to demonstrate the significant effect of roughness on the transport of hydrocarbon liquids in ultra-confined carbon pores. As a surrogate model of shale rock, a pristine carbon slit pore, with a pore height of 3 nm, was divided into five smaller blocks of equal size which were rearranged to create two different family of structures, ridged and stepped pores, while maintaining the pore height. The rough pores were characterised by a rugosity ratio, $C\phi/R$.

Transport of binary mixtures of n-octane and n-hexadecane was investigated at 300 bar and 300 K, using a boundary driven NEMD technique which provided transport

diffusivities, permeabilities and Onsager coefficients from a single set of simulations. Each species was modelled as a chain of tangentially bonded coarse-grained spherical monomers, with the monomers interacting using a Mie potential. The models are robust and accurately predict both thermodynamic and transport properties of C_8 and C_{16} . A particular advantage of this type of coarse-graining is that a molecular based equation of state, SAFT- γ Mie, can be used to efficiently determine pressures and chemical potentials from the two bulk reservoirs in contact with the pores from BD-NEMD simulations.

To validate and complement the results of BD-NEMD, additional EqMD and EF-NEMD simulations were also carried out. From EqMD simulations, it was seen that the pores are not selective to either hydrocarbons and the adsorbed densities matched bulk densities at different pressures. At the conditions studied, adsorption does not significantly affect transport. However, BD-NEMD simulations indicate that rugosity can reduce transport diffusivities by up to three orders of magnitude, and that there are two rugosity-related linear regimes in the observed transport diffusivities. In pores of several nm wide, transport is dominated by the characteristics of the flow in the middle of the pore (as opposed to the surface regions). For smooth slit/straight pores, the flow is relatively fast whereas for very corrugated pores, the pore geometry dominates transport suggesting to the emergence of regions dominated by diffusive flow, leading to overall slower transport. Moreover, rugosity induces regions of stagnant fluid which slow the rest of the fluid down, leading to curved velocity profiles.

No transport selectivity is observed for the systems studied. Independent of pore type, both species flow together and have the same velocity. Although the self-terms of the transport diffusivity matrix indicate a faster self-transport diffusivity of octane relative to n-hexadecane, it should not be assumed that octane flows faster as the large values of the cross coefficients indicate a high degree of mutualisation. As expected, the total flow speed is dependent on composition and the transport of the fluid is slowed down with increasing n-hexadecane content. Darcy's law is applicable for the systems studied, as permeabilities are only dependent on pore geometry and are

independent of fluid composition. Permeability of the slit pore is in the order of μD , being 3 orders of magnitude larger than fluid permeabilities observed in organic shales (nD). We conclude that the slit carbon pore model, albeit useful to study adsorption, is an unrealistic geometry to study transport in shales.²⁴⁸ Even a small level of surface imperfections (rugosity) decreases transport by several orders of magnitude, rendering stepped rugose mesopores as sensible candidates to study transport in organic shales, given the low permeabilities of 10 nD.

Finally, it has been demonstrated that collective and self-diffusivities are orders of magnitude smaller than transport diffusivities, and thus one must be careful in using self-diffusivities as the sole metric to describe the transport of dense fluids inside pores similar to those presented in this work. Particularly for mixtures, using self-diffusivities to predict transport selectivities is not correct as the cross correlations are not taken into account.

Chapter 6

Effect of surface roughness and morphology on the adsorption and transport of CH₄/CO₂ mixtures in nanoporous carbons

6.1 Introduction

Shale gas, a mixture of CH₄ (> 94%), higher hydrocarbons and inorganic gases, is an important unconventional fuel that exists in the porous structure of kerogen rocks.²⁴⁹ As the world shifts to a prospect of sustainability, the sum of shale gas reservoirs discovered globally is now five times more than those of conventional nature, providing an alternative to less clean fossil fuels such as coal.²⁵⁰ Despite its abundance, shale gas extraction is challenged by the intrinsically low permeability of kerogen.^{5,6} This is improved by various fracturing techniques used to create fissiles in kerogen which allow shale gas to exit the porous structure via diffusion.^{7,8} Among these techniques, a method with a promising environmental prospect is CO₂ fracturing. This method exploits the strong adsorption property of CO₂ displacing

CH₄ out of confinement,^{251–253} and the injected CO₂ can then be stored safely in depleted reservoirs under stable geological conditions, further making it a plausible CO₂ sequestration technique.^{254–256} Due to those positive outlooks, the study of transport of CH₄/CO₂ mixtures in nanoporous environments has enjoyed much interest from researchers.^{257–259} Thus understanding fluid transport in nanopores is of paramount importance.

Classically, pressure-driven flow is described by the Navier-Stokes equation and the Hagen-Poiseuille equation which treat fluids as continuum bulks. This assumption works well for macro-confinement, but performs poorly with microscopic confinement. Holt et al.⁵³ showed that flux in carbon nanotubes is five times faster than the prediction of the conventional models. This is because under nano-confinement, solid-fluid interactions become an important factor that affects transport behaviour. At this scale, recognizing the discrete (molecular) aspect of matter becomes critical to modelling and predicting transport. The Knudsen and Dusty-gas^{260,261} models are examples of theoretical models at this scale, but much work is needed for those theories to be predictive. Computer simulations have played a pivotal role in elucidating the role that confinement has in the modes of transport in confinement. In macro-pores (pore size > 3 nm),^{28,39,47} the perceived picture is of convective flow and well-defined parabolic velocity profiles.⁴⁸ In meso-pores (pore size > 1 nm), the solid-fluid interactions near the wall induce dense adsorption layers which contribute to slip at the wall and fast transport. In micro-pores (pore size < 1 nm) fluid transport is dominated by diffusion.⁵¹ Readers are referred to Roque-Malherbe⁸² for an excellent summary of the transport mechanism in porous media.

Although theory can describe transport in porous media using ideal surrogate models, understanding transport in realistic pores characterised by complex porosity and tortuosity becomes less obvious from a theoretical point of view. Imaging techniques such as scanning electron microscope (SEM) and nano-computed tomography (nano-CT) have been used to study the characteristics of porous shales.²⁶² Klaver et al.²⁶³ and Guo et al.²⁶⁴ generated 3D models of shale rocks using SEM

methods. Their results demonstrated a large variance in pore characteristics, including a convoluted network of tortuous pathways and diverging channels. They conclude on the importance of capturing solid morphism in any attempt to model transport.

A large amount of research has been dedicated to studying carbon-based solids as they are highly relevant in gas separation and ubiquitous in organic matrix-related work.⁵² Common representations of carbon pores include carbon slit pores and carbon nanotubes (CNTs), both of which have ideal smooth surfaces.^{53–55} Kazemi and Takbiri-Borujeni^{39,40} studied the flow of methane in perfect carbon slit pores at 300K and 330 atm. They observed fast plug-like transport which has been repeatedly reported in the literature. Jin and Firoozabadi^{56,57} generated flow in a smooth graphene slit pore using dual control volume grand canonical molecular dynamics. They reported faster transport than the prediction of Hagen-Poiseuille model and attributed the difference to the mobile adsorption layers. Similar scenarios have been discussed by Riewchotisakul et al.⁵⁸ and Wang et al.²³³ using mobile pistons and external force fields to induce flow in carbon slit pores. In all of those reports and other similar ones, we speculate that there is a cause-effect relationship between surface smoothness and this unexpected fast plug flow. Castez et al.⁴⁷ investigated into this issue by randomising the distribution of carbon particles to generate atomic-scale roughness in carbon nanotubes. They showed that rugosity slows down the transport significantly. Similarly, Castez et al.⁴⁷ studied methane transport in carbon nano-pores with atomic-scaled roughness. They reported a significant drop in near-surface fluid velocity, which associates rugosity with surface friction that hinders the overall transport. He et al.⁴⁹ studied the effect of large-scale roughness on methane transport in graphite pores and noted the disruptions of the parabola velocity profile. Phan and Striolo²⁸ added solids blocks inside slit pores to generate a collection of pores with various characteristic parameters. Their results demonstrated a linear relationship between methane transport and the pore characteristic parameter. Finally, Fayaz-Torshizi et al.⁹⁰ studied the transport of hydrocarbons in stepped and ridged pores. One of the key conclusions is that smooth pores are inadequate to represent the

complexities of flow through natural nanoporous environments and their use actually leads to spurious results.

From the aforementioned studies, a general conclusion that can be garnered is that surface roughness in mesopores does indeed have a significant effect on transport. However, few studies have focused on multicomponent mixtures and how surface roughness affects their transport behaviour.^{59,60} Zhu et al.⁶¹ studied the transport diffusion mechanism of CH₄/CO₂ mixtures in shale nanopores. They observed that CO₂ injection weakens the CH₄ surface diffusion and reported the critical rule of pore size in determining the transport mechanism. Sun et al.⁶² investigated the competitive adsorption of CH₄/CO₂ mixtures in shale matrix. They reported significant effect of pressure and rugosity on competitive adsorption. Finally, Collell et al.³⁰ and Vasileiadis et al.²⁶⁵ investigated the adsorption and transport behaviour of hydrocarbon mixtures in kerogen. Those studies focus on realistic models of shale pores, which are difficult to characterize and/or systematically modify. Hence it is impossible to deconvolute the effects of the solid structure from other effects, such as the surface chemistry. The major challenges of those studies are two fold: The lack of metrics to define pore characteristics that affect transport, and the necessary tools to effectively calculate the transport properties. This work takes interest in how rugosity affects the transport of CH₄/CO₂ mixtures, by defining metrics for pore characteristics as well as utilising efficient tools to measure transport properties. Boundary-Driven Non-Equilibrium Molecular Dynamic (BD-NEMD)²⁵ is used to study the transport behaviour of pure methane and CH₄/CO₂ mixture on two types of rugose carbon pores.

6.2 Methodology

6.2.1 Rugose slit model

Pore construction

Carbon solids are modelled as graphite sheets, the structure of which has been illustrated in Chapter 2 (Figure 2.7).

Generating rugosity

To generate rugose surfaces, we developed an algorithm that adds or removes coronene-shaped clusters on surfaces until the rugosity reaches $\pm 0.01\text{nm}$ of a target value. The algorithm maintains structural integrity, ensuring a realistic structure and constant solid density, e.g. no floating atoms nor voids within the solid are allowed.

The resulting solid consists of a maximum of 14 graphene sheets. The four outer layers on both sides are active sheets, meaning they are subjected to modification to create rugosity. The inner three layers are pristine for structural integrity. The thickness of the base layers exceeds the cut-off radius to prevent adsorbed fluids from interacting through the wall. An illustration is shown in Figure 6.1, where grey carbons represent the base layers and red represents the active layers. The smooth pore is the starting point of the algorithm and has two active layers switched on prior to modification.

Rugosity is quantified using Equation 6.1 where n is the number of carbon particles on the surface, x_i is the height of carbon i , x_{mean} is the averaged surface height.

$$R = \sqrt{\frac{\sum_{i=1}^n (x_i - x_{mean})^2}{n}} \quad (6.1)$$

Accessible volume

Porosity is generated by lifting the top boundary by a distance H to create free volume in the system. Due to the periodic boundary condition, the free volume forms a

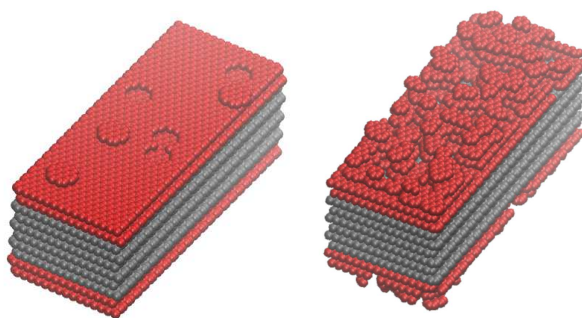


Figure 6.1: Cartoon of coronene addition/removal on graphene layer, target rugosity set at $R = 0.075$ (left) and $R = 0.5$ (right).

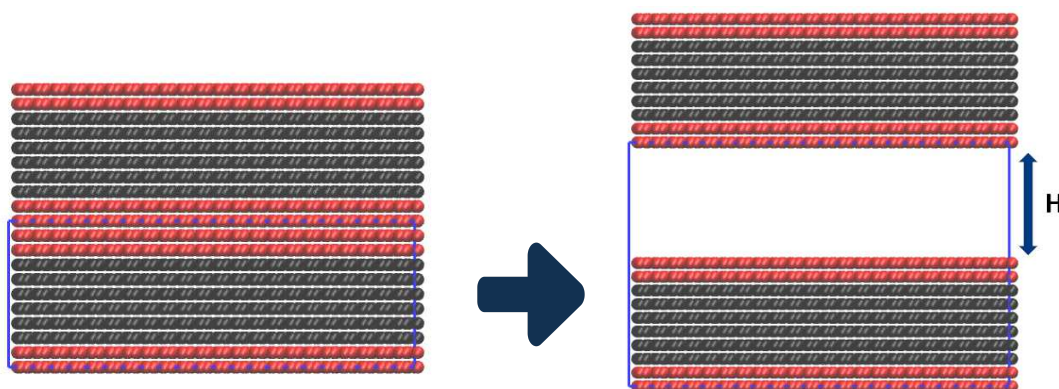


Figure 6.2: An illustration to highlight the production of a pore of height H in a smooth slit pore (left).

channel with a height of H . The definition of pore height is ambiguous between research, as different reference points can be employed (e.g. center-to-center distance between adsorbed molecules or center-to-center distance between solid atoms in opposing surfaces) Here H is defined as the pore height and refers to the effective distance between the apparent surfaces of the atoms on opposing surfaces. The same process can be applied to a rugose structure by lifting the top boundary from the average surface level.

In this chapter, the periodic boundary of the smooth solid is lifted by 3 nm. To maintain a constant pore volume, intuition suggests that the boundary of other solids should be treated the same way. However, this conjecture is false because some volume pockets at the rugose surface are too small for fluid to access. Lifting the boundary of a rugose solid by the same height would result in smaller effective pore volumes. Therefore, individual treatments are required and the accessible volume V_A ,

was evaluated using "Pore Blazer" packages²⁶⁶ with methane probes. Figure 6.4 shows that at constant H , accessible volume decreases with rugosity due to the increasing number of inaccessible volume pockets. Therefore, a scaled value of H was determined for each individual solid to compensate for the difference. A list of the H values and the accessible volume of rugose pores is presented in Table 6.1 .

Rugosity Levels	Parameters			
	Pre V_A / nm ³	Scaled H / nm	Post V_A / nm ³	System Height x / nm
0	91.82	3.000	91.82	6.06
0.025	91.85	3.003	91.71	6.06
0.05	91.82	3.000	91.49	6.06
0.1	90.59	3.035	91.73	6.09
0.2	87.26	3.165	91.33	6.22
0.3	83.28	3.325	91.23	6.38
0.4	78.84	3.403	90.71	6.46
0.5	75.14	3.439	90.69	6.60

Table 6.1: Summary of pre-scaled accessible volume, scaled pore height H and post-scaled accessible volume of different rugose pores. The pre-scaled V_A assumes a unscaled $H = 3\text{nm}$. The dimension of the simulation cells are 9.45nm (length), 6.06nm (width) and H nm (Height)

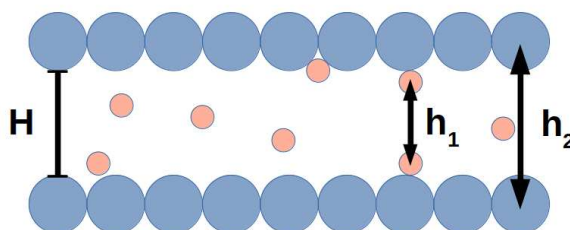


Figure 6.3: An illustration to distinguish between the pore height definition of choice (H) to other definitions such as: center-to-center distance between adsorbed molecules(h_1) or center-to-center distance between solid atoms in opposing surfaces(h_2)

6.2.2 Coronene fragments model

Pore construction

To set up this structure, simulation boxes filled with different densities of coronene-fragments are simulated at 1000 K under NVT ensemble. The fragments

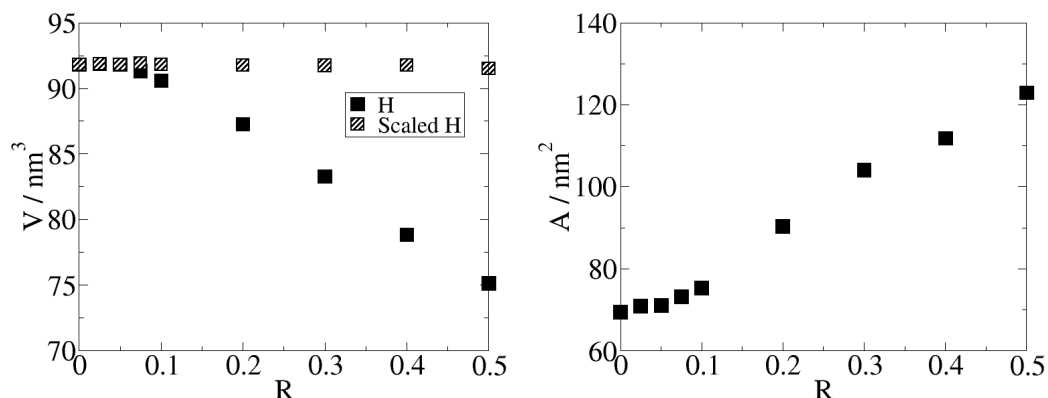


Figure 6.4: Summary of accessible volume V (left) and accessible surface area A (right) using methane probe at different rugosity levels R . Using a constant uniform value of H results in a decaying accessible volume as rugosity is increased (black symbols). A scaled value of H is used to retain a constant accessible volume at different rugosity levels (grey symbols).

undergo random thermal motion and their instantaneous configuration at the end of the simulation is recorded. The solid is restrained against this configuration with a harmonic constant of $10,000 \text{ kJ mol}^{-1} \text{ nm}^{-2}$. Solid-solid interactions are turned off for thermostat purposes. Two representative examples are shown in Figure 6.6. The pore size distribution of the coronene fragment model was assessed using PoreBlazer.²⁶⁶ The majority of the pore size lies below 30 nm and we observe a steady decrease in the mean size as the number of fragment increases. (Figure 6.5)

Solid characterization

Arguably, the coronene fragment model has a richer and wider configuration space. The single, unidirectional channel in the rugose slit model is substituted by a collection of interconnected tortuous paths. As a result, the path length between two points tends to be several times longer than the straight distance. To describe this character, the concept of tortuosity τ was introduced by Carman^{267, 268} as the ratio between the effective flow path L_{eff} length to the straight distance L . This concept scales up the length in porous media and can be interpreted as transport resistivity.

$$\tau = \frac{L_{eff}}{L} \quad (6.2)$$

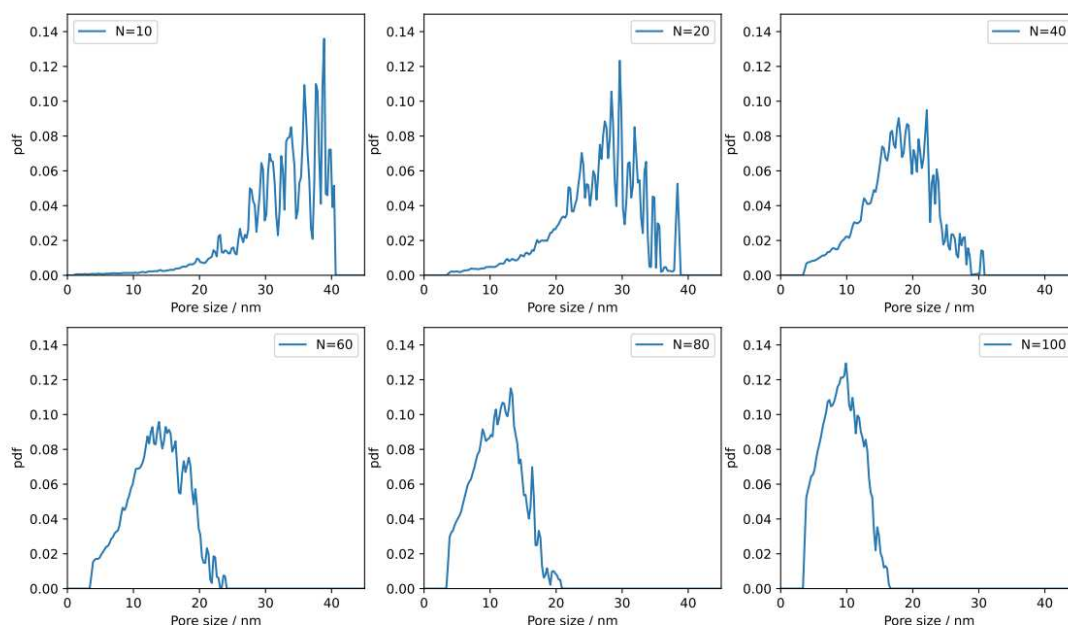


Figure 6.5: Pore size distribution of the Coronene Fragment model at different solid density. The distribution is evaluated using PoreBlazer package and CH₄ as probe. The distribution is averaged over 20 realisation of the pore structure.

Historically, the lack of understanding of tortuosity led to significant discrepancies in modelling transport in capillary tubes. Because of the intrinsic difficulties in measuring this quantity, there are several methods to yield an estimation of tortuosity from porosity for some classes of materials.^{269,270} However, the performance of those over-simplified methods has often been limited.²⁷¹ In this chapter, tortuosity is measured directly using molecular dynamics. A methane probe is placed at the pore entry and allowed to roam inside the pore. The path length upon its exit is averaged and compared with the shortest distance. Naturally, there are statistical errors associated with this method. A particular probe may find a linear path by chance or be trapped in a dead end for an inordinately long period of time. Analysis shows that the path length follows a lognormal distribution, with a sharper peak with increasing sample size.(Figure 6.7) To reduce the variance of our estimator, path sampling is repeated until the standard error is less than 1 nm.

The restriction and divergence of pore channels add variety to pore size

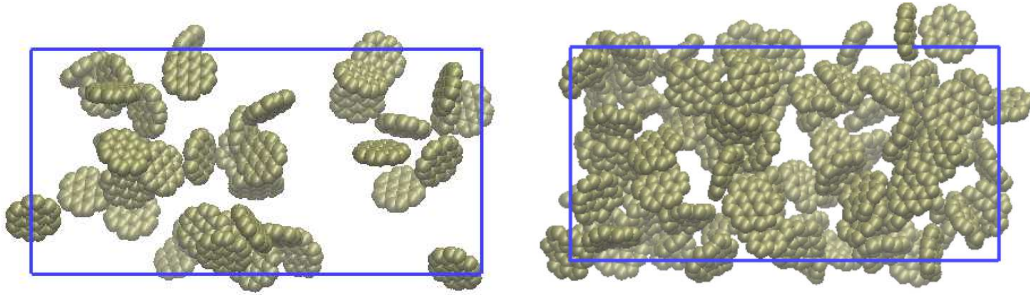


Figure 6.6: Snapshots of coronene fragments model. Example shown of $N = 40$ (left) and $N = 120$ (right) coronene sheets respectively. Carbon atoms vibrate around an equilibrium position and the periodic boundary conditions are applied in the direction in and out of the page. The illustrated cells have the following dimension: 8 nm (length), 4 nm (width), 4 nm (depth).

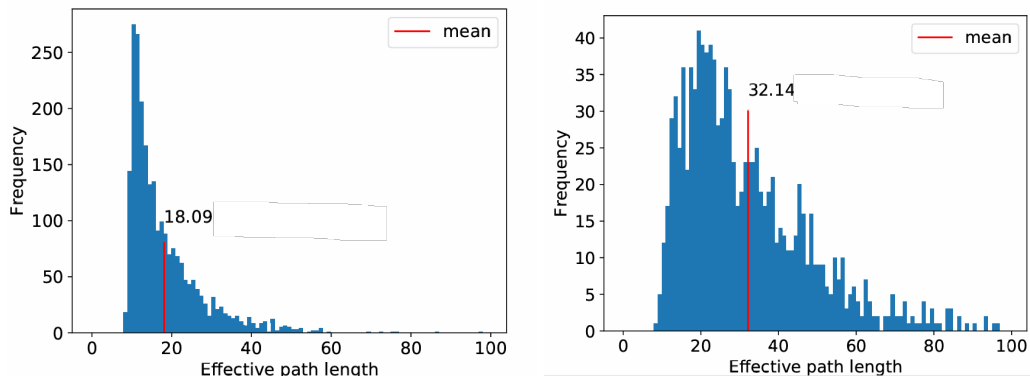
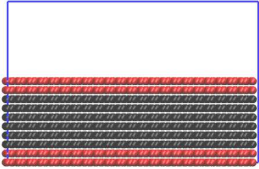
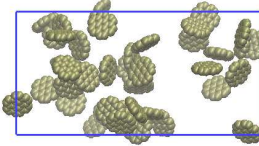


Figure 6.7: The effective path length L_{eff} of methane molecule in $N=10$ (left) Coronene fragment pore and $N=100$ (right) Coronene fragment pore. The red line represents the mean whose ratio with the pore length is defined as tortuosity. Path length is measured in nanometers.

Table 6.2: Characteristics parameters of the pore structures employed in this study.

Pore Type		ϕ	τ	c	$c\phi/\tau$
Rugose slit 	R=0	0.441	1.938	1.000	0.228
	R=0.025	0.440	1.954	0.885	0.200
	R=0.05	0.439	1.983	0.884	0.196
	R=0.1	0.438	2.139	0.805	0.165
	R=0.2	0.427	2.234	0.752	0.144
	R=0.3	0.415	2.470	0.714	0.120
	R=0.4	0.408	2.542	0.717	0.115
	R=0.5	0.400	2.651	0.732	0.110
Coronene fragment 	N=10	0.980	2.586	0.998	0.378
	N=20	0.960	2.784	0.978	0.337
	N=40	0.918	3.150	0.902	0.262
	N=60	0.876	3.515	0.803	0.200
	N=80	0.828	4.102	0.689	0.139
	N=100	0.781	4.631	0.604	0.102

distribution and bring more complexity to the structure. This feature is described by the constriction factor c and it is represented as the ratio between the average and the maximum restriction size. The pore structures are sliced perpendicularly to the direction of transport, and the porous sizes in each slice are measured. A small value of c describes a large variance in the size distribution.

The porosity, ϕ , is the fraction of accessible pore space V_A to total volume V , defined as

$$\phi = \frac{V_A}{V} \quad (6.3)$$

Although pore characteristics such as tortuosity, constriction factor and porosity are often discussed together, it is essential to recognise their independent nature. This argument is supported by Schwartz et al.²⁷² and Bear et al.²⁷³, who showed that the effect of different characteristics can be separated for any porous medium. A collection of pore characteristics of both models are summarised in Table 6.2.

Table 6.3: Mie potential parameters.

Species		Interaction Parameters		
i	j	λ_{ij}	$\varepsilon_{ij}/k_B / \text{K}$	σ_{ij} / nm
Methane (M) ²⁰³	M	16.4	170.8	0.375
Carbon dioxide (C) ²⁰³	C	14.65	194.9	0.285
Wall (W) ¹⁰²	W	12.0	28.0	0.340
M	W	13.977	68.9	0.3576
C	W	13.24	73.0	0.31
M	C	15.49	177.3	0.33

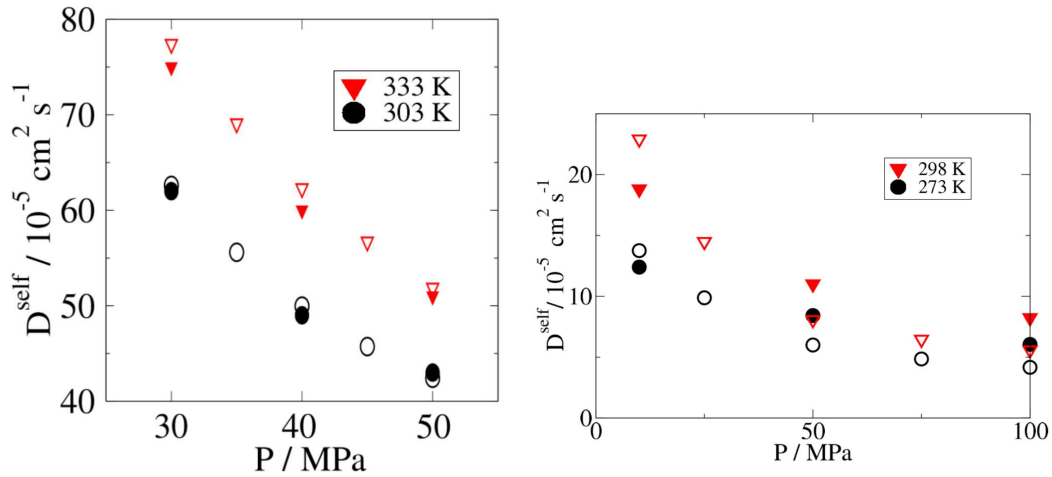


Figure 6.8: Self diffusivity of CH_4 (left) and CO_2 (right) predicted using MD simulations (empty symbols) as compared with literature (filled symbols). For CH_4 , triangles and circles correspond to $T = 333 \text{ K}$, and $T = 303 \text{ K}$. For CO_2 , triangles and circles correspond to $T = 298 \text{ K}$, and $T = 273 \text{ K}$.

6.2.3 Molecular interactions

Inter-molecular interaction in this chapter is modelled by a set of Mie potential, whose parameters were generated via a top-down coarse-graining method.²⁷⁴ Methane is modelled as single sphere molecule and carbon dioxide as double tangent spheres molecules. The detailed simulation parameters are presented in Table 6.3.

To demonstrate the validity of this model, self-diffusivity was simulated and compared to experimental data. Figure 6.8 shows the fluid model successfully captures experimental self-diffusivity at a range of conditions,^{205,275} which justifies the use of those parameters to study transport. Solid (carbon) potential values are taken from the parametrization of Steele.¹⁰²

6.2.4 Simulation Details

The simulation box dimensions for rugose slit pores are fixed at 32.45 nm in length and 3.64 nm in width. Within this, a solid structure spans 9.45 nm, enclosed by 11.5 nm bulk regions on either side. While maintaining constant length and width across all simulations, the height is adjusted to accommodate variations in accessible volume (Figure 6.4). The simulation box dimensions for the coronene fragment pores are 31 nm in length, 4 nm in width, and 4 nm in height. An 8 nm-long solid region is positioned between two bulk regions, each measuring 11.5 nm in length.

Fluid particles were added and simulations are performed in the canonical (NVT) ensemble for 2 million steps of 2 fs. Once the fluids are equilibrated inside the pore, the force field at the boundary region is activated and BD-NEMD simulations are run in the NVT_w ensemble. It is important to point out that T_w symbolizes that the temperature coupling is only applied to the wall particles. To achieve this, the solid particles are allowed to vibrate around an equilibrium position using a harmonic oscillator, with a bonding potential of $10,000 \text{ kJ mol}^{-1} \text{ nm}^{-2}$. Excessive energy from the force field is discharged through fluid-solid interactions to keep the fluid temperature constant. For the coronene fragment models, every solid particle is available for interaction with the fluid. In this case, the solid-solid interaction is turned off to remove the strong repulsive force. However, the same strategy will not work for slit pores because the inner graphene layers can not interact with fluids. Instead, the solid-solid interaction potential in slit pores is limited to $r < 3.8 \text{ nm}$. This allows interaction between graphene layers for energy removal. Each BD-NEMD simulation was run for 20 million time-steps of 2 fs. The first 15 ns of the simulation were used to reach a steady state, while the remaining 25 ns were used for analysis. Each system is run ten times using different accelerations ranging from 0 - 0.04 nm ps^{-2} to improve statistics. The centre of mass motion removal feature is turned off. Cut-off radius is 1.5 nm in all simulations.

BD-NEMD simulations are run using a modified version of GROMACS/5.1.2¹⁹⁴ and combined to GROMACS/2018.¹⁹⁵ Simulation visualisations are rendered using the

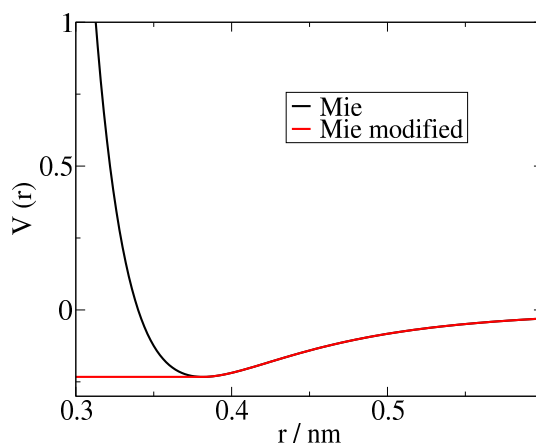


Figure 6.9: Regular Mie potential of solid interaction (Black) and truncated Mie potential (Red). The truncated potential is used in NEMD simulations for effective thermostates

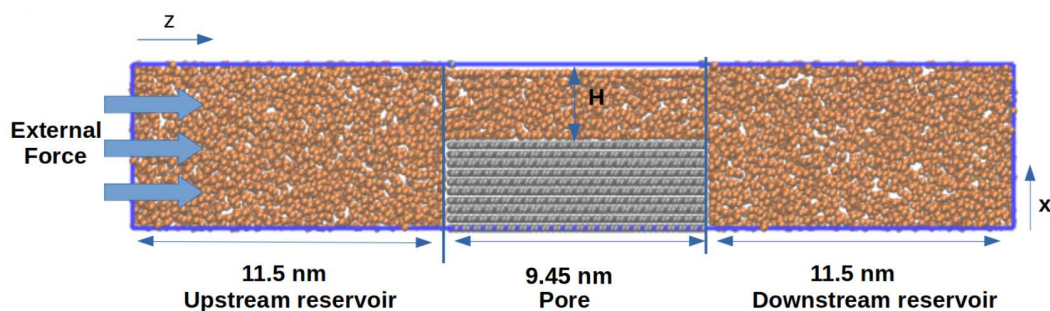


Figure 6.10: An illustration of a boundary-driven non-equilibrium molecular dynamics (BD-NEMD) simulation applied to a slit graphene pore. $R = 0$.

VMD package.¹⁹⁶

6.3 Results

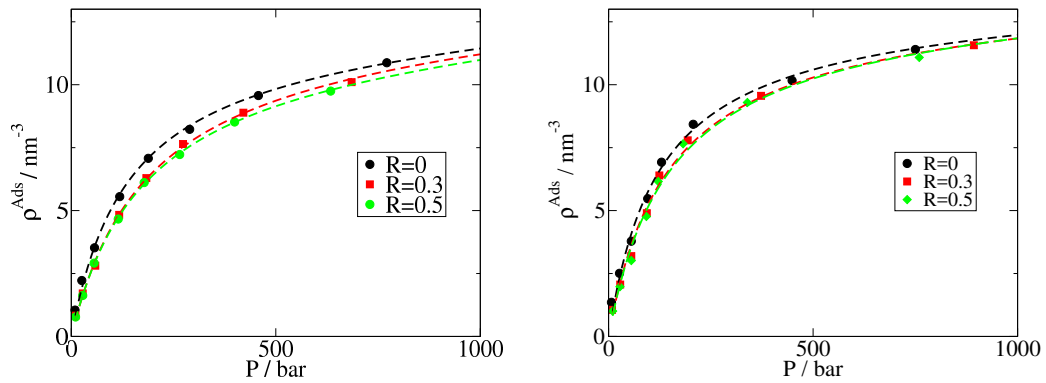
6.3.1 Slit Pore

Adsorption isotherm of pure fluids

Pure CH_4 and CO_2 are equilibrated with both smooth and rugose pores to assess how rugosity affects adsorption. Simulations are run from the dilute limit to a high-pressure (density) region. After the fluid is introduced in the cell, equilibrium molecular dynamics were run for 2 million steps with a step size of 2 fs. Temperature

Table 6.4: BET parameters for adsorption isotherms modelling.

Cases		BET Parameters		
Fluid	R	M	k_a	k_b
CH ₄	0	16.4	170.8	0.375
CH ₄	0.3	12.0	28.0	0.340
CH ₄	0.5	13.977	68.9	0.3576
CO ₂	0	16.4	170.8	0.375
CO ₂	0.3	12.0	28.0	0.340
CO ₂	0.5	13.977	68.9	0.3576

**Figure 6.11:** CH₄ (left) and CO₂ (right) adsorption isotherms at three different rugosity level in slit pores, simulation data (symbol) are fitted using the BET model (dashed lines). T = 298 K.

coupling is applied to maintain the fluid at 298 K using v-rescale thermostat. Simulation results were fitted using BET model (Equation 6.4) and the parameters are presented in Table 6.4.

$$n_i^o(P) = M \frac{K_A P}{(1 - K_B)(1 - K_B + K_A P)} \quad (6.4)$$

Adsorption isotherms of pure CH₄ and CO₂ are plotted in Figure 6.11. In all cases, the density of the adsorbed fluid ρ^{Ads} rises sharply as the overall pressure increases, following a type *I* adsorption behaviour. In the high-pressure region, the isotherms appear saturated. When comparing rugosity levels isobarically, the plot shows a mild drop in ρ^{Ads} , suggesting rugosity weakens adsorption. This observation seems controversial because rugosity is usually associated with stronger adsorption due to the

increased surface and availability of high-energy defects.²⁴⁶ To answer this, a clear understanding of the density distributions at the near-wall region is essential. Figure 6.12 compares the adsorbed density profiles in the x direction (from wall to wall) at varying rugosity. Adsorbed density is averaged along an yz plane and $x = 0$ represents the mid-point between the two walls. It is shown that rugosity has no effect on the density near the $x = 0$ region, which is unsurprising as the fluid-solid interaction is minimal here. With increasing x , well-defined density peaks are found in smooth pores and the plot suggested the presence of two distinct adsorption layers. In contrast, the density peaks in rugose pores are scattered and decay rapidly with increasing x . The integrated area below the density profile for the rugose models is smaller than that of the smooth slit, which suggests that the adsorption in rugose pores is less efficient. Further visualisation shows that fluid molecules form a dense hexagonal lattice on a smooth surface. This arrangement maximises surface usage and leads to high adsorption and is a consequence of the unusually large tangential pressure exerted on the fluid.²⁷⁶ This orderly and the consequent high local pressure is an artefact of the ideal geometry and would be very unlikely in any natural pore. Fluids are unable to pack efficiently in rugose pores, resulting in reduced adsorption despite a larger surface.

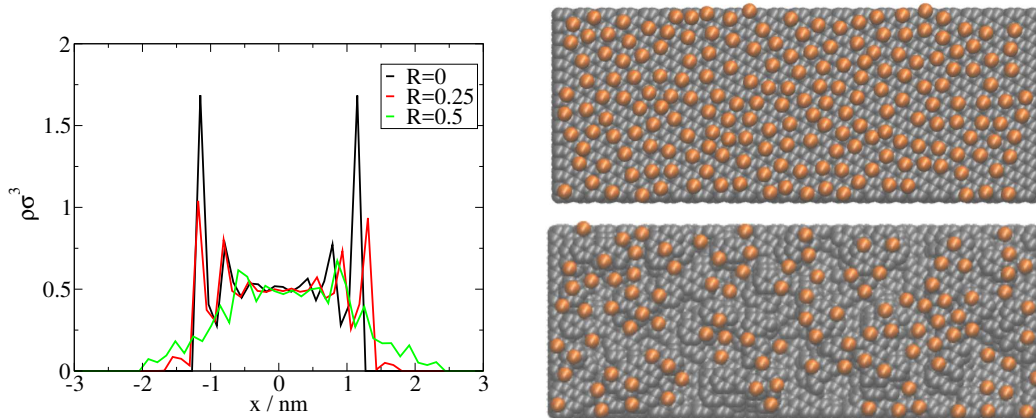


Figure 6.12: Adsorbed CH_4 density profile at different rugosity levels. x represents the distance from the centre of the slit. $\rho\sigma^3$ is the reduced CH_4 density. A more organised surface density pattern is observed for the smooth pore (top right) as compared to a pore of $R = 0.5$ (bottom right). $T = 298 \text{ K}$.

Transport diffusivity of pure fluids

Figure 6.14 shows the relation between transport diffusivity D^t , global density ρ and rugosity R . Global density refers to the ratio between the total number of molecules in the system with respect to the total volume of the system. The need to define this quantity arises from the fact that in a BD-NEMD, the bulk density is ill-defined, as it differs between the upstream and downstream. Furthermore, during the set-up of the system, a number of molecules will eventually be adsorbed. Hence the use of the global density is a more consistent way to communicate fluid loading. A negative correlation is found between transport diffusivity and rugosity. This correlation can be partially explained by the weakened adsorption caused by rugosity. However, the principal driving factors are the increased friction and the disruption of plug-flow that accompany the enhanced rugosity. Velocity maps generated from EF-NEMD on infinite pores show a uniform velocity distribution within smooth pores. The introduction of rugosity slows the fluid near the wall and significantly disrupts the flow pattern from the wall to the centre of the flow. The difference in average fluid velocity contributes to the change in transport diffusivity. Lastly, the dense, mobile adsorption layers found in smooth pore contributes greatly to the overall transport. The fluid is seen to have "no-slip" when exposed to the pristine carbon surface, leading to enhanced transport. The same condition does not apply to rugose pores. Not only are the surface adsorbed molecules scattered, but their collective motion is also disturbed by the rugose environment. Adsorbed particles may also be trapped in the narrow valleys formed by the solid, and remain there for the entire simulation. The velocity heat map in Figure 6.13 demonstrates the piston-like flow in smooth pores, in contrast to the parabolic-like velocity profile in rugose pores.

The study was repeated on carbon dioxide under the same conditions. Figure 6.11 and Figure 6.14 report the CO_2 adsorption isotherms and transport diffusivity. The simulation shows stronger adsorption and faster transport for CO_2 , but otherwise very similar qualitative behaviour.

It is worth noting that due to the stochastic pore-generating method, a certain rugosity level can manifest in different forms (or realisations) of pore structures. Those

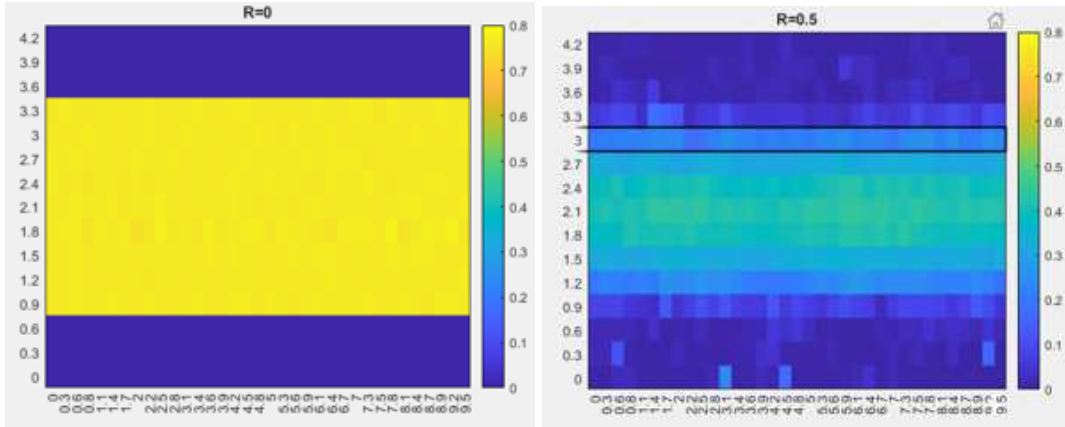


Figure 6.13: CH₄ velocity distribution in roguse slit pores of rugosity $R = 0$ (left) and $R = 0.5$ (right). Velocity is averaged over the course of the simulation.

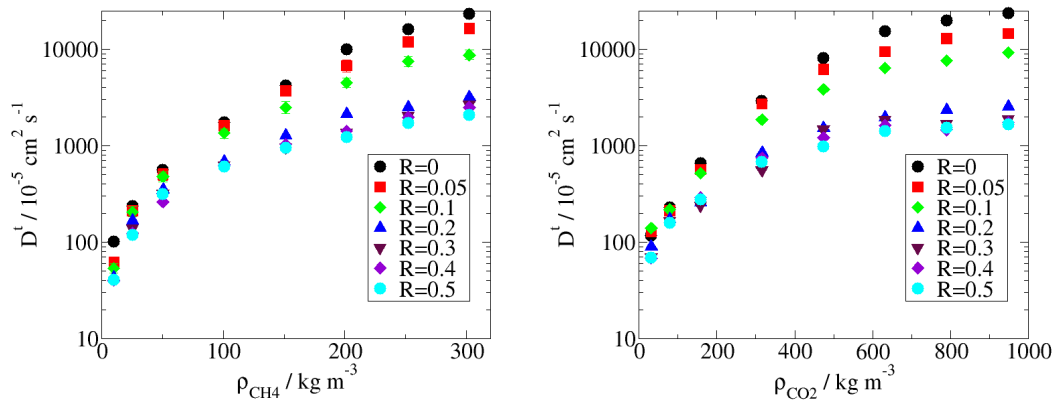


Figure 6.14: Summary of CH₄ (left) and CO₂ (right) transport coefficients D^t at different rugosity level R . System ranges from the diluted limit to high density, $T = 298$ K. Error bars are within the size of the symbols

differences can lead to different transport behaviour and it is important to evaluate their effect. Figure 6.15 shows the CH₄ transport diffusivity under 20 realisations of rugosity levels at different densities. BD-NEMD is run with a single acceleration $F = 0.04 \text{ nm ps}^{-2}$ and transport diffusivity is obtained by estimating the β_1 of a linear regression model through the origin.²³⁷

Selectivity of CH₄/CO₂ mixture

CH₄/CO₂ mixtures were used to study adsorption selectivity at different rugosity levels. Simulations were run at different molar compositions (ranges from 10% CO₂ to 90% CO₂) while maintaining an initial (no acceleration) equilibrium bulk pressure of

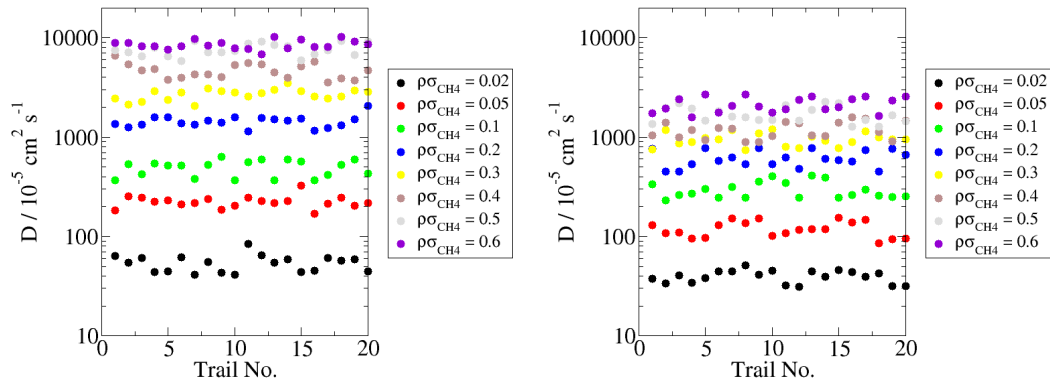


Figure 6.15: CH₄ transport diffusivity measured under different realisation of solid with rugosity level $R = 0.1$ (left) and $R = 0.5$ (right). $T=298\text{K}$.

100 bar. A Python implementation of the gSAFT package²⁷⁷ and SGTpy²⁰⁶ is used to compute the density of the mixture that meets the composition and pressure conditions. After equilibrating the system in NVT_w ensemble, the coexisting bulk density and the adsorbed density for CH₄ and CO₂ are obtained. Adsorption selectivity $S_{CO_2}^{Ads}$ is calculated by comparing the bulk to adsorbed density ratio of the two fluids.

$$S_{CO_2}^{Ads} = \frac{\rho_{CO_2}^{Ads}}{\rho_{CH_4}^{Ads}} \bigg/ \frac{\rho_{CO_2}^{Bulk}}{\rho_{CH_4}^{Bulk}} \quad (6.5)$$

Figure 6.16 reveals that CO₂ has stronger adsorption than CH₄ at all fluid compositions. Nevertheless, rugosity is shown to consistently reduce the CO₂ adsorption advantage. As the surfaces transit from smooth pore ($R = 0$) to a high level of rugosity ($R = 0.5$), CO₂ adsorption selectivity drops from 1.5 to 1.2. This suggests that the use of a smooth pore as a surrogate for carbonaceous pores (or kerogens) will provide spurious results and overestimate the CO₂ adsorption and the effect of competitive adsorption advantages on CH₄ production enhancement. A related question is the effect of rugosity on transport selectivity. Infinite pore EF-NEMD is employed to obtain the flux ratio which is compared to the adsorption density ratio to compute the CO₂ transport selectivity $S_{CO_2}^T$.

$$S_{CO_2}^T = \frac{J_{CO_2}}{J_{CH_4}} \bigg/ \frac{\rho_{CO_2}^{Ads}}{\rho_{CH_4}^{Ads}} \quad (6.6)$$

In this case, we observe an enhanced CO_2 transport selectivity due to rugosity, suggesting CO_2 has a faster transport in a rugose pore.

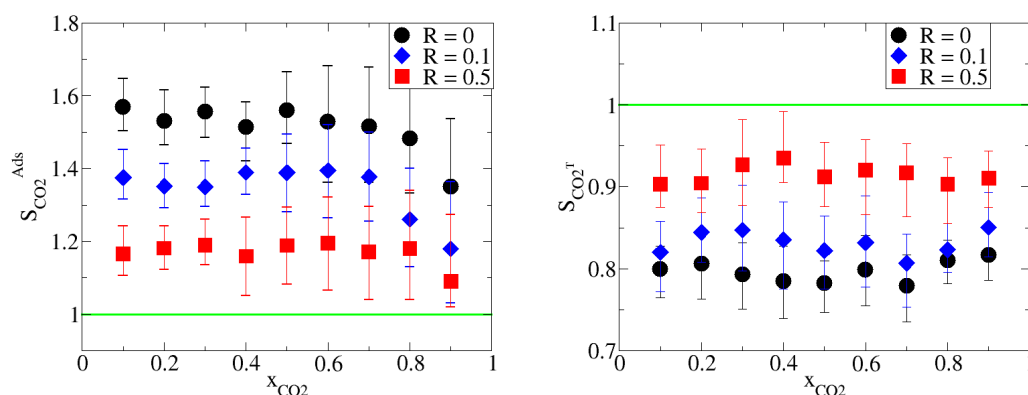


Figure 6.16: Adsorption selectivity (left) and transport selectivity (right) of carbon dioxide in smooth pore ($R = 0$) and rugose pores ($R = 0.5$) at different molar compositions. Bulk equilibrium pressure is maintained at 100 bar for all cases shown, $T = 298$ K.

6.3.2 Coronene fragment model

Adsorption

Adsorption isotherms for CH_4 are determined at different equilibrium bulk pressures up to 500 bar at 298 K. Stronger methane adsorption is observed with an increasing number of fragments. To study the adsorption selectivity, CH_4/CO_2 mixtures with a range of composition are simulated at 100 bar and 500 bar. Figure 6.17 shows that the pore is more selective towards CO_2 at low pressure and less selective at high pressure. The magnitude of decrease in selectivity appears to be correlated with the number of coronene fragments N . By comparing the accessible volume for CH_4 and CO_2 , it is seen that CH_4 can occupy up to 20% more volume than CO_2 due to the size and shape difference (Figure 6.18). This effect is particularly prominent when high-pressure fluid is paired with a dense solid, therefore causing a significant selectivity reduction at high N values. The variance of the simulation result can be attributed to the randomness of the solid structure. Figure 6.18 shows the adsorption selectivity measured from different realizations of the coronene fragment pores. The results from different realizations were

averaged and show a positive correlation between $S_{CO_2}^{Ads}$ and coronene number N at low pressure.

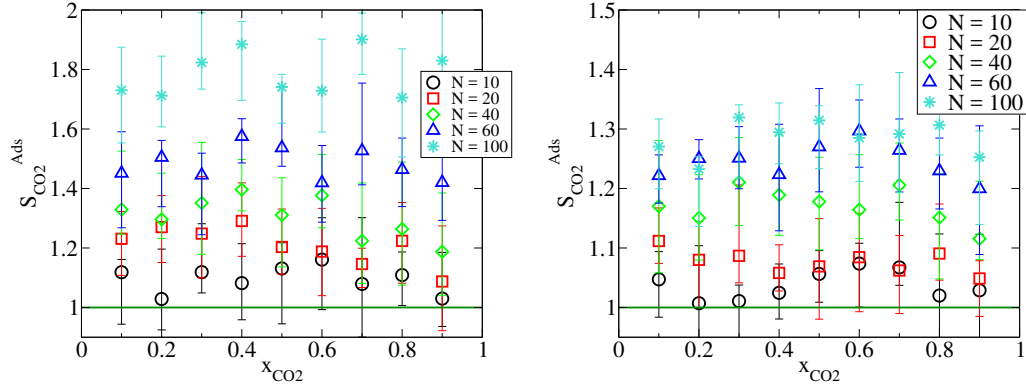


Figure 6.17: CO₂ adsorption selectivity at 100 bar (left) and at 500 bar (right) of CO₂ in various Coronene fragment pores at different molar compositions. T = 298 K.

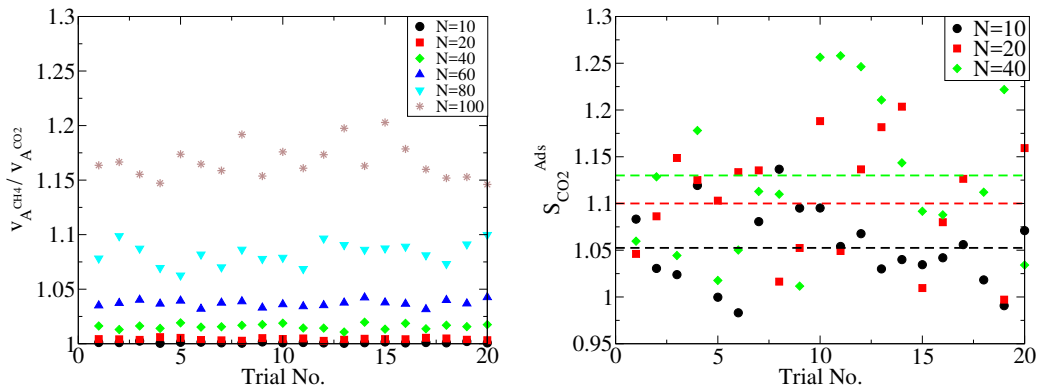


Figure 6.18: Variation of accessible volume ratio between CH₄ and CO₂ (left) and variation of CO₂ adsorption selectivity (right) of CO₂ in different realisations of coronene fragment pores. The dashed horizontal line represents the mean value. Bulk pressure is maintained at 100 bar for adsorption selectivity, CO₂ composition is 0.5, T = 298 K.

Transport

Employing BD-NEMD, the transport diffusivity of CH₄ is evaluated by relating the observed flux to the density gradient inside the pore. The results are shown in Figure 6.19. Transport in pores with minimum coronene solid is much faster than the dense ones, with two orders of magnitude reduction from the highest porosity to the lowest. We

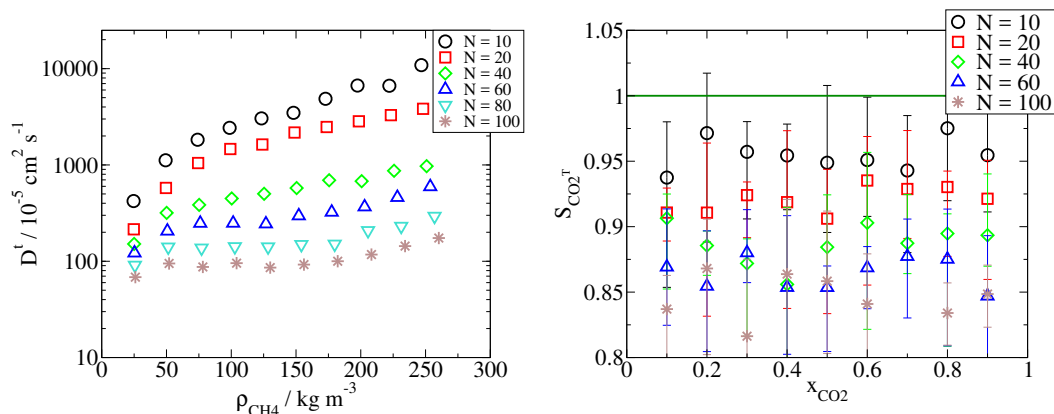


Figure 6.19: Summary of CH₄ transport diffusivity D' in coronene fragments pores. Results obtained from a set of BD-NEMD simulations at different fluid and solid densities, $T = 298 \text{ K}$ (Left). CO₂ transport selectivity at 100 bar in various coronene fragment pores at different molar compositions. $T = 298 \text{ K}$ (right).

observe that the complexity brought by the use of coronene fragment pores far exceeds that of the rugose slit pore. The high tortuosity exhibited by the former induces a non-uniform flow pattern in coronene fragment pores. Similar patterns were observed for the transport selectivity, $S_{\text{CO}_2}^T$ decreases with the increasing number of coronene N .

Characteristic factor

The models for carbon pores employed here exhibit contrasting characteristics due to their structural difference. For the rugose slit pore model, rugosity is generated by adding or removing carbon clusters at a fixed orientation. The essentially straight flow channel of the underlying slit pore is preserved and the flow path does not differ significantly between pores. Therefore, increasing surface rugosity has a lower impact on porosity, tortuosity, and constriction factors. In contrast, the coronene fragment pores consist of a randomized collection of carbon clusters at randomized orientations, where a freely available pore channel is unavailable even at low solid densities. The overall characteristic of the coronene fragment model is more reminiscent of a natural structure such as kerogen, while the slit pore model is a closer match to a graphitic carbon.^{99,278} It is seen that large constriction factors and high porosities are favourable to transport, and tortuosity decreases transport, therefore it seems reasonable to

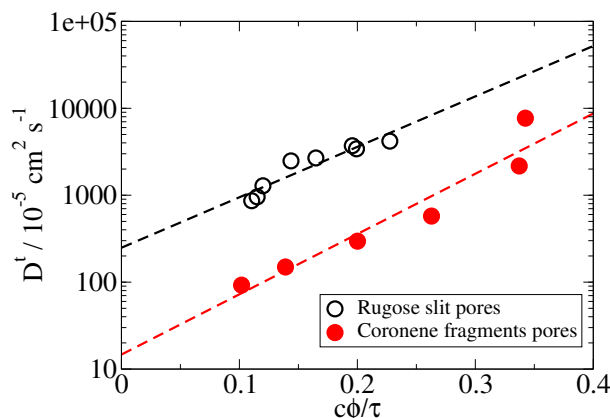


Figure 6.20: Apparent correlation between CH_4 transport diffusivity D^t and characteristic factor $c\phi/\tau$ rugose slit pores (black) and coronene fragment pores (red). Each data point represents a different pore configuration. CH_4 is at a reduced global density of 0.3, $T = 298 \text{ K}$. A linear best-fit curve is shown by the dashed lines.

consider $D^t \propto c\phi/\tau$. This empirical relationship has been proposed by Phan and Striolo^{28,279,280} as an empirical variable capable of being used to map pores of disparate morphologies into a single correlation. Figure 6.20 shows the transport diffusivity of methane at a reduced density of 0.3 in a number of pores studied. By plotting transport diffusivities against the characteristic factor $c\phi/\tau$ on a logarithmic scale, a linear correlation can be observed in both the rugose slit pore model and coronene fragment model. This evidences the correlative power of the characteristic factor within a specific solid model family. However, it would be challenging to reach a generalisation using characteristic factors alone. As Figure 6.20 demonstrates that the two models are disconnected and it is crucial to identify the fundamental structural difference between pores.

6.4 Conclusions

The aim of this chapter was to investigate how rugosity and pore characteristics affect the transport behaviour of CH_4 and CO_2 in carbon pores. Transport of pure fluid and

CH₄/CO₂ binary mixture were investigated at 298 K using boundary-driven NEMD techniques. Inter-molecular interactions are described by a set of Mie potentials, which was shown to accurately capture the thermodynamics and transport behaviour of the fluids. The Mie parameters allow the use of a molecular-based equation of state SAFT- γ Mie to effectively calculate bulk properties, thus linking the molecular details to macroscopic properties. Fluids are simulated in two different carbon pore models: rugose slit pores and coronene fragment models.

For rugose slit pores, simulation on the pure fluids shows that surface rugosity has a detrimental effect on fluid adsorption. Because fluids can arrange themselves more effectively on a smooth surface, the formation of compact adsorbed layers ultimately led to a negative correlation between rugosity and adsorption. This decrease in adsorption partially leads to a slower transport in the rugose pore, and we report that rugosity can decrease the transport by an order in magnitude. Moreover, fluid transport in smooth nanopores is reported as a fast plug flow, yet even a small instance of surface rugosity modifies significantly the fluid velocity profile which will exhibit a parabolic profile with non-slip at the surface. In terms of CH₄/CO₂ mixtures, we observe strong CO₂ adsorption compared to CH₄ in the slit pores, which agrees with previous results in the literature. In a rugose pore, CO₂ has a weakened adsorption advantage. As for transport selectivity, the study shows that CO₂ conversely has higher transport selectivity in a rugose pore.

Overall, similar qualitative trends are exhibited by the coronene fragment models, where the transport drops by two orders of magnitude with increasing solid density and CO₂ is shown to have stronger adsorption only at low pressure. Differences between the models are attributed to the difference in their structural nature. Lastly, we have seen that correlating transport with characteristic factors alone yields different results for the two models studied here, highlighting the importance of distinguishing and categorizing solid structures.

We suggest that the smooth surface models may overestimate the CO₂ adsorption and underestimate the CO₂ transport, both of which are important metrics used in

evaluating the performance of CO₂ fracturing and sequestration. We stress that the use of graphitic smooth slit carbon pores models are unsuitable to study transport in natural carbonaceous deposits or kerogens.

Chapter 7

Conclusions and Future Work

7.1 Conclusions

At the start of this document, we stressed the importance of incorporating the suitable methodology to evaluate fluid transport in nano-scaled pores. This document revisited the boundary-driven molecular modelling strategy to evaluate mass transport coefficients of fluids in nanoconfined media. By comparing BD-NEMD values with EqMD results, it revealed that the current assumption of calculating concentration gradients using bulk reservoir concentrations can lead to inaccurate results for the transport diffusivity. Using the concentration of the adsorbed fluid as reference for the concentration gradients, the BD-NEMD method was shown to provide results in accordance to EqMD, but with less uncertainty. This thesis also introduced a novel approach to evaluate Darken correction factors for systems with Mie potentials, using the SAFT- γ Mie equation of state instead of relying on simulations. For dense fluids and liquids, transport coefficients were found to be significantly larger than self diffusivities, challenging the common assumption of their equivalence. In addition, the

use of the boundary-driven molecular modelling strategy is expanded to multi-component fluids. In binary systems, the impact of adsorption selectivity on transport was minimal, while particle size played a more pronounced role. Larger particles dominated transport, resulting in mutualized flow in slit pores with no transport selectivity.

We noticed in the literature a lack of understanding on the effect of surface rugosity on transport. To address this, this thesis reports the results of modelling the transport of n-octane and n-hexadecane and their mixtures through carbonaceous nanopores at high-pressure conditions. We find that smooth slit carbon pore models, which are commonly employed in literature as surrogates for kerogen regions in shale, are an inadequate representation of ultra-confined natural pores. For slit pores, the flow patterns are characterized by a fully-mutualized plug-like flow and extremely fast transport. However, by incorporating even a small amount of rugosity (roughness) to the solid walls, the diffusion coefficients decrease dramatically with surface roughness significantly affecting the characteristic transport and velocity profiles inside the pores. In all cases, it is seen that there are important cross-correlation effects, influencing the way components of the mixture flow together. In this particular application, we again see that calculated self-diffusivities are orders of magnitude smaller than the observed transport diffusivities for liquid mixtures.

The transport behavior of CH_4/CO_2 binary mixture in rugose slit pores and coronene fragment pores were investigated, revealing a significant disruption of the flow of CH_4 and CO_2 in both of those rugose solid models. The study suggests that the smooth surface models overestimate the CO_2 adsorption and underestimate the CO_2 transport, both of which are important metrics used in evaluating the performance of CO_2 fracturing and sequestration. In addition we have seen that correlating transport with characteristic factors alone yields different results for the two models studied here, highlighting the importance of distinguishing and categorizing solid structures and the lack of any apparent "universality" in the correlations. The study again emphasizes the need to move beyond smooth surface models and consider rugosity for

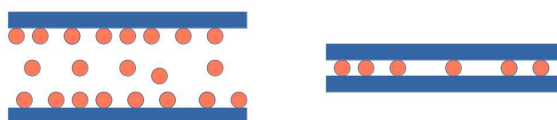


Figure 7.1: Illustration to show the arrangement of adsorbed fluid in wide and narrow slit pores.

realistic assessments of fluid transport in natural carbonaceous deposits and kerogens.

7.2 Directions for future work

7.2.1 Applicability of BD-NEMD for very narrow pores

Most of the pores considered in this document have a size of 3 nm. In these pores, the fluid near the surface forms adsorption layers, while molecules in the middle of the pore experience minimal interaction with the solid. As the pore size decreases, the dimension of the unaffected stream diminishes. In the limit, the pore can become so narrow that only one fluid particle can pass through at a time. In those cases, the transport mechanism diverges from the cases studied in this document, and the accuracy of BD-NEMD in evaluating transport in this setting has not been investigated thus far.

7.2.2 Applicability of BD-NEMD for high density Coronene fragment pore

The Coronene fragment pore is defined by the density of Coronene, with a maximum of 100 Coronene fragments presented in this document ($N = 100$). It has been noted that BD-NEMD faces challenges when applied to pores with $N > 150$. This difficulty is mainly attributed to the existence of a dense Coronene matrix, which impedes flow and substantially increase the tortuosity. In this setting, the observed flux was generally small and displays poor statistics. While this issue can be partially mitigated by increasing the acceleration step, such adjustments make the simulation unstable and pose challenges in maintaining an effective thermostat. The condition resembles that

mentioned section 7.2.1, but is aggravated by the fact that there might not even be a free pathway between the upstream and downstream.

The current construction method relies on randomly freezing the Coronene fragments in place, a more structured method that ensure minimum passageways could potentially solve this issue. Similarly, a realistic kerogen structure might experience swelling of the matrix by the fluid, more complex scenarios would require a new set of models and simulation techniques.

7.2.3 Water in Shales

In hydraulic fracturing, high pressure water is injected into the well to create fissures within the shale matrix.²⁸¹ The recovery of injected water during this process is typically limited in the flowback, with a significant portion remaining in the reservoir. This residual water is believed to undergo imbibition into the matrix. Due to the capillary discontinuity between the matrix and the fracture, water blockage forms near the matrix/fracture interface, leading to a reduction in hydrocarbon relative permeability. Consequently, shut-in operations are frequently implemented immediately after hydraulic fracturing to mitigate water blockage by redistributing the water deeper into the reservoir through capillary imbibition.²⁸²

There are two types of pores in a typical shale reservoirs: large pores within the organic matrix (kerogen) and small pores within the inorganic clay matrix (Fig 7.2). The prominent contributors to total shale porosity are the interconnected large organic pores, characterized by substantial bodies and small pore throats. These pores exhibit oil-wet characteristics, indicating that water has with no affinity for the pore surfaces. In contrast, the small pores with water-wet characteristics have water coating the walls. This duality in surface affinity imparts a combination of oil-wet and water-wet wettability characteristics to shale-gas reservoirs.²⁸³

The tools outlined in the document can be utilized to explore the behavior of water within a mixed organic pore (carbon) and an inorganic pore (silica/clay). Additionally, they offer the capability to assess the effectiveness of pressurized water in 'flushing out'

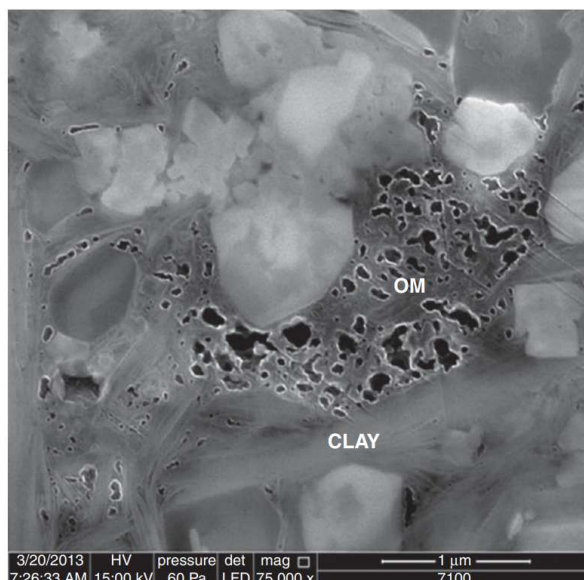


Figure 7.2: SEM image showing organic matter (OM) in a Utica shale sample. The diameter of the large pores is approximately 200 nm. Clay pallets surround the organic matter. Because of their hydrophilic nature, the clay pores attract the water from the larger organic pores.²⁸³

adsorbed methane and the efficacy of those procedures in different pore types.

7.2.4 Effect of thermostats on BD-NEMD

In this thesis, BD-NEMD simulations are performed using the NVT_w ensemble with the velocity rescale thermostat applied to solid. It would be beneficial to conduct a systematic study on the impact of various thermostat settings on these simulations. For instance, exploring how the BD-NEMD method might be affected by applying a gradual thermostat to fluids or investigating the variation in results with different thermostat configurations, such as using a different random seed. Such an analysis could provide deeper insights into the robustness and reliability of the BD-NEMD method.

7.2.5 Further investigation on fluid-solid interaction

In Case III of Chapter 3, a fluid with modified interactions with the solid was introduced, demonstrating the applicability of BD-NEMD to binary fluid systems. To further this investigation, it would be beneficial to explore a broader range of

parameters when examining the adsorption of molecules with varying interactions with the solid. Additionally, introducing repulsive sites on the solid surface could provide valuable insights, allowing us to study whether BD-NEMD can accurately capture these interactions.

7.3 Publication

The following manuscripts have derived from the work presented in this thesis.

- Use of Boundary-Driven Nonequilibrium Molecular Dynamics for Determining Transport Diffusivities of Multicomponent Mixtures in Nanoporous Materials (2022).²³⁷ The thesis holder contributed in the writing and research of this study, and independently performed the research of Case II and Case III as a co-author.
- Significant Effect of Rugosity on Transport of Hydrocarbon Liquids in Carbonaceous Nanopores(2022).⁹⁰The thesis holder contributed in the writing and research of this study, and produced and verified results in section 5.3 as a co-author.
- Effect of Surface Roughness and Morphology on the Adsorption and Transport of CH₄/CO₂ (2023).²⁸⁴ The thesis holder contributed in the writing and research of this study as the first author.

7.4 Posters and Presentation

Some elements of this thesis have been presented in the following meetings.

- The use of BD-NEMD on the study of fluid transport in rugous nano-confinement, Thermodynamics conference, University of Bath, 7-9 September 2022.
- The use of NEMD to evaluate transport diffusivity in nano-confinement, 5th UK porous materials conference, Glasgow, 13-14 June 2022.

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