Development and implementation of the generalized continuum model for transport in porous media

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Thesis for the Degree of Philosophiae Doctor (PhD)
University of Bergen, Norway
2018

UNIVERSITY OF BERGEN

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Date of defence: 19.03.2018

Year: 2018

Title: Development and implementation of the generalized continuum model for transport in porous media

Name: Leonid Vasilyev

Print: Skipnes Kommunikasjon / University of Bergen

Preface

This dessertation is submitted as a partial fulfillment of the training program for the degree Doctor of Philosophy (Ph.D.) at the University of Bergen. The advisory committee consisted of Florin Adrian Radu (University of Bergen), Kundan Kumar (University of Bergen) and Jan Martin Nordbotten (University of Bergen). The project has been supported by the Research Council of Norway under grant 178013: "'Geological Storage of CO2: Mathematical Modeling and Risk Assessment"'.

Acknowledgements

First, I would like to thank my advisers at the University of Bergen for their time and effort spent guiding me during my time as a Ph.D. candidate. The dissertation would never have been completed without the guidance of my main supervisor Adrian Florin Radu. I am also very thankful to my co-supervisor Jan Martin Nordbotten for sharing his inspiration and expert knowledge with me, when it was especially needed. It was also very beneficial to have discussions and meetings with my co-supervisor Kundan Kumar. His curiosity and questions forced me to look deeply into details and, therefore, helped me to understand the problem better. It has been a privilege to work with such a superior team that believed in both me and our work.

The financial support from the Research Council of Norway (# 178013) is also highly appreciated.

Finally, I would like to thank my family for their care and support, and for providing me the luxury to complete this work.

Nomenclature

ADE	Advection-Dispersion Equation
BTC	Breakthrough Curve
CTRW	Continuous Time Random Walk model
FDE	Fractional Differential Equation
GCT	Generalized Continuum Transport model
GME	Generalized Master Equation
MRMT	Multi-Rate Mass Transfer model
REV	Representative Elementary Volume
TPL	Truncated Power Law for the CTRW model

Abstract

Fluid flow phenomena in porous media have always attracted a lot of attention of scientists and engineers. Attempts to quantify the average transport in homogeneous media with a simple partial differential equation with constant coefficients disclosed significant inconsistencies comparing to experiments. Modern numerical simulations of porous networks confirmed that those inconsistencies are systematic and not caused by the observation error. The error appeared as a result of the, so called, anomalous or non-Fickian transport, which was in contrast to the normal regime, described by the Fick's laws.

The problem has been addressed through the introduction of more complex and substantial models to describe the phenomena. Although, these new approaches have resolved the problem of quantification, they have raised another question for researchers and engineers, how to choose the most suitable approach and, if it is possible, to parametrize the modeling choice at all. The models general lack of physical consistency makes it difficult to distinguish the model parameters. This leaves judging of suitability to the general accuracy of quantification only, which is often not the most important criterion. In other words, the model parameters are typically estimated by fitting the model to the experimental data, and are often not related to the real properties of the medium. Therefore, a model is often chosen a priory, based only on the experience of the researcher.

In this work, we address the problem of model selection by introducing a new model: the Generalized Continuum Transport model. This model transforms into existing models at certain limits and, therefore, constrains the modeling choice through the introduction of the parameter space. It is shown that the Generalized Continuum Transport model limits to the advection-dispersion equation, the Continuous Time Random Walk, the Multi-Rate Mass Transfer and the Multiple-Porosity models, when corresponding configurations of the parameter space are applied.

The model's accuracy is studied by quantifying the breakthrough curves obtained from a fine scale porous network modeldemonstrating significant appearance of anomalous transport phenomena. The results show that the error of quantification is smaller than the error of the existing models.

It is discussed that the parameters of the Generalized Continuum Transport model are related to the physical properties of porous media. Finally, it is presented that the parameter space of GCT can be constrained and related to the transport phenomena studied. Hence, the limits of GCT are controlled by the transport complexity and the desired accuracy and the modeling choice can be parametrized.

Outline

This dissertation consists of two parts. In the first part a background theory is provided for the papers included in the second part. Part I is structured as follows. Chapter 1 contains a brief description of porous systems and fine scale approaches for modeling transport phenomena on a pore level. In Chapter 2, the appearance of non-Fickian transport is introduced as opposed to normal or Fickian. Existing large scale modeling approaches for transport in porous media are presented in Chapter 3 starting from the most simple models and moving towards more sophisticated and more accurate approaches. The included papers are summarized in Chapter 4.

The following papers are included in the thesis as Part II:

Paper A: J. Nordbotten and L. Vasilyev. On the relationship between multiple porosity models and continuous time random walk. In proceedings of XVIII International Conference on Water Resources CMWR2010, 2010.

Paper B: L. Vasilyev, A. Raoof, and J. M. Nordbotten. Effect of mean network coordination number on dispersivity characteristics. Transport in Porous Media, 95(2):447–463, 2012.

Paper C: L. Vasilyev, J. M. Nordbotten, A. F. Radu, and K. Kumar. On the properties of the parameter space of the generalized continuum transport model for description of fluid flow in porous networks. Transport in Porous Media, 119(3):673–688, 2017.

Paper D: L. Vasilyev and A. F. Radu. On the ability of the Generalized Continuum Transport Model to properly capture dispersion. Accepted for publication in Analele Stiintifice ale Universitatii Ovidius Constanta, Seria Matematica, 2017.

Contents

Part I

Background

Chapter 1

Introduction

"Look deep into nature, and then you will understand everything better."
–Albert Einstein

Our physical knowledge of the laws of nature is based on observations and experiments. Mathematical modeling is the way to quantify a physical phenomenon or, in other words, the method to relate physical quantities to each other. There always exist a gap between our understanding of the processes underlying the phenomenon and the mathematical model describing it. A mathematical model can perfectly quantify the phenomenon but, at the same time, it may lack the knowledge of the underlying process or interpret the process in an unnatural manner. On the other hand, a model can demonstrate good description of the dominating physical phenomenon, while omission of some minor effects may lead to poor quantification.

Modeling of flow through porous media has always been challenging for scientists, even though the porous systems have usually been considered simplified and idealized. On larger scales, the fundamental laws of physics are not sufficient to provide a closed form system. Experimental or phenomenological relations, such as Hooke's law, Darcy's law or Fick's laws, were derived in order to represent a system within a single scale.

Porous media can, without exaggeration, be found everywhere. Generally, any medium that can be penetrated by fluids is a porous medium. Therefore, the applications of flow models are potentially numerous. Leakage through concrete can flood a house basement or destroy a dam, tidal waves enter sand and affect groundwater. Accurate models are especially important for enhanced oil recovery and hydrology.

Porous media are, by nature, essentially heterogeneous. It is, though, possible, to some extent, to treat a large porous block as homogeneous, if its properties remain roughly unchanged on that scale. For decades, scientists and engineers used the Advection-Dispersion Equation (ADE) and its variants for transport quantification. The model is very reliable and easy to use, it is easily solvable both numerically and, more important, analytically. ADE has also been adopted for more complex geometries by introducing variable coefficients or additional source-leak terms.

ADE is still commonly used also nowadays, despite that even the early idealized laboratory flow tests on homogeneous systems demonstrated systematic deviations that could not be explained by inaccurate measurements [Aronofsky and Heller, 1957,

Scheidegger, 1959, Silliman and Simpson, 1987]. Many authors related these deviations to the existence of preferential flow paths related to the porous structure or textural differences [Ehlers, 1975, Bouma, 1981, Beven and Germann, 1982, Brusseau and Rao, 1990, Wang, 1991, Thoma et al., 1992, Flury et al., 1994, Liu et al., 1998, Pruess, 1999]. The results of these preferential paths are, for example, fingering [Hill and Parlange, 1972, Hillel, 1987] or funneled flow [Kung, 1990, Steenhuis et al., 1990, Walter et al., 2000]. Neuweiler and Vogel [2007] estimated the effective unsaturated parameters for non-Gaussian heterogeneous porous media which reflected the existence of connected paths for different parameter ranges. It was demonstrated, that connectivity of different parameter ranges contains important information that determines the typical time scales of the flow process [Neuweiler et al., 2011]. In contrast to the previous findings, Ghodrati and Jury [1992] reported the occurrence of preferential flow even in apparently "structureless" soils at the field scale. Systematic deviations appeared as long tails in breakthrough curves (BTCs) and, due to this, the phenomenon was called *"the tailing effect"*. Such transport is often referred as anomalous or non-Fickian in contrast to normal, Gaussian or Fickian which satisfies the Fick's laws of diffusion. In principle, any transport phenomena that cannot be quantified with ADE can be referred to as anomalous.

A common issue that appears when modeling transport in random systems is the increase of dispersion with the scale of observation. The increase of the dispersion coefficient from Darcy scale to laboratory scale and to field scale was reported by measuring the BTCs and extracting the dispersion coefficient using different methods like fitting of ADE and calculation of the second spatial moment [Fried, 1975, Cushman, 1986, Suciu, 2014].

ADE treats "homogeneous" media under some assumptions, though this homogeneity rarely, if ever, can be found in nature. In natural geological formations heterogeneities are present at all scales and can refer to the distribution of geometrical properties (porosity, pore conduction, coordination number), variation of biogeochemical properties of the medium that affects the passing fluid (wall friction, reactions with the medium), or even variation of fluid characteristics (reactions, viscosity, diffusion).

It was, therefore, logical to employ probabilistic approaches to quantify the appearance of non-Fickian behavior. In past years, much attention was paid to the Continuous Time Random Walk (CTRW) framework [Kenkre et al., 1973, Shlesinger, 1974, Berkowitz et al., 2006]. This approach treats a porous medium as a grid of discrete sites, where fluid particles or, in other words, small volumes can reside. Transition from site to site is defined through a transition time and the transition time distribution. Thus, the information about the medium's properties is summarized into the distribution, which is not directly related to the medium's physical characteristics. Despite the lack of knowledge about the system and the discrete nature of CTRW unsuitable for mathematical investigation, it inspired a variety of deeper analyses. This resulted in the development of the random walk based or equivalent models, such as Multi-Rate Mass Transfer [Dentz and Berkowitz, 2003], fractional ADE [Hilfer, 2000, Metzler et al., 1998], Global Random Walk [Vamoş et al., 2001, Suciu et al., 2011].

Another direction of investigations focused on further development of ADE in order to account for the medium's properties variations on different scales. Here, two major approaches stand out. The first one is the introduction of space, time and concentration dependent coefficients of ADE. The second approach, of a special interest for the work

presented in this thesis, introduces also a scale dependency of coefficients such that ADE transforms into a system of two or more equations: dual and multiple porosity models [Gerke and Genuchten, 1993, Gwo et al., 1996].

For a model of a physical phenomenon, all aspects of the selected model are important and determine the modeling choice. But they are not equally preferable for different problems. If the purpose is to quantify a laboratory or numerical experiment, then accuracy plays the major role. If the medium's characteristics are to be obtained, then it is reasonable to use a model, which parameters represent or directly related to the physically observable properties. For mathematical investigations, model's continuity may be important, while accuracy and physical consistency can suffer.

Another challenge appears in the modeling choice itself. Determination of the correct complexity of the transport equations and the parameter space constraints are often made a priory, based only on the experience and the desire of a researcher. Parameters of the model are typically estimated from tests, thus BTCs, or even fitted. But they may not be related to the medium's characteristics. It is, therefore, beneficial to have a model which complexity is parametrized and where the parameter space can be constrained based on the medium's properties.

In this thesis, we give an overview of the existing deterministic and stochastic approaches to modeling transport in porous media. The models are discussed and compared in terms of their accuracy of anomalous transport prediction, suitability for mathematical investigations and physical consistency of the parameters.

Much attention is paid to the appearance of non-Fickian phenomena in homogeneous synthetic porous networks, constructed such, that they reproduce a realistic random structure of real porous systems as proposed in Raoof and Hassanizadeh [2010]. Large scale models are discussed in terms of their ability to quantify the appearance of the "tailing effect" in BTCs.

Finally, a new approach, called *the Generalized Continuum Transport model* (GCT), is introduced in the thesis as a new robust and attractive framework for transport quantification and mathematical investigations. The difficulty of model selection is addressed by appealing to the fine scale models of transport processes, and the macroscale parameters of GCT are extracted from the medium's characteristics. The parameter space of GCT is considered through its limits to classical models: ADE, CTRW, MRMT and multiple-porosity. It is demonstrated, how the model complexity and the parameters of GCT are related to the pore network parameters and the velocity field. Thus, the construction of the parameter space eliminates the issue of modeling choice and provides correlation to the medium's nature.

Another interesting feature of GCT presented in this work is the adaptivity of the GCT model to the complexity of transport phenomena and the desired accuracy. It is demonstrated, that the size of the parameter space and, hence, the complexity of equations can automatically adjust to transport complexity, and all necessary effects, such as non-Fickian phenomena, are captured only if they appear. For example, no extra calculation is needed when a plume has passed and the concentration remains stable.

The main contributions of this work are summarized below:

1. **Simulation of non-Fickian behavior in homogeneous porous networks.** We model transport in homogeneous porous networks with randomly constructed

pore space according to Raoof and Hassanizadeh [2010] which corresponds to real porous media. Fine scale simulations provide information about the porous networks and the breakthrough curves for future analysis. Parameters of the networks and the velocity field are extracted from the simulations and translated into the GCT's parameter space. The BTCs are investigated in terms of appearance of "the long tails" as the result of non-Fickian behavior in a system on the macroscale.

2. **Formulation of the Generalized Continuum Transport model.** The GCT model is introduced and its parameter space is presented. Important limits to the classical models are obtained by constraining the parameter space. Numerical approaches for the GCT assessment are suggested.

3. **Relation of the GCT parameter space to pore network characteristics.** An important aspect of any large scale model is the possibility to obtain its parameters from macro and microscale properties of the porous medium. Typically, the parameters are estimated by fitting the breakthrough curves. In this case a laboratory test or a numerical simulation has to be performed. Alternatively, empirical correlations can be derived. It is, therefore, beneficial to extract the parameters directly from the information about the medium. It is shown that the parameter space of GCT can be directly derived from the velocity distribution, which is related to the distribution of the microscale properties of the network. At the current stage BTCs are still needed in order to obtain some important parameters (this is discussed in Chapters 4.6, 4.7, Papers C and D), but we believe that in the future it will become possible to avoid large scale simulations at all.

4. **Parametrization of the modeling choice: GCT adaptivity to transport complexity.** It is shown that the construction of the GCT parameter space can be parametrized and related to the complexity of transport phenomena modeled. Parametrization of the parameter space eliminates the problem of model selection, and the complexity of equations can be determined by the expected or observed transport complexity. It is always a trade off between accuracy and computational efforts, but it is favorable to constrain the modeling choice to a set of some meaningful parameters. This becomes possible with GCT.

Chapter 2

Brief introduction to flow in porous media

"Science is beautiful when it makes simple explanations of phenomena or connections between different observations."
–Stephen Hawking

Flow through porous media is a broad topic that can be encountered in many fields of industrial and scientific interest including ground water hydrology, reservoir modeling, geothermal energy and carbon dioxide storage. Examples of porous materials can be found almost everywhere and include soils, porous and fractured rocks, filtering paper, sand, ceramics and concrete. Considering these examples, it is possible to imagine, how systematization and characterization of porous media are useful, and how accurate quantification of transport is important. In this chapter, we present some basics of porous media and an approach for accurate numerical representation of porous media on a fine-scale.

2.1 Flow in porous media

A porous medium can intuitively be defined as a solid material with holes or pores in it. Though this definition is very straightforward, it has a few points missing. It is crucial to understand the concept of a continuum through which a fluid can flow. Therefore, the pores should be interconnected, that it can be established several continuous paths between two sides of the medium. Moreover, it should be a possibility to exchange fluid between the paths. We follow Bear et al. [1968] to define a porous medium as:

1. a portion of space occupied by a multiphase matter, where at least one phase is not solid. The space within the domain that does not comprise the solid part is called the void space;

2. the solid phase should be distributed throughout the porous medium such that it is present inside each representative elementary volume (the meaning of a representative elementary volume is explained below);

3. some of the pores should be interconnected creating the effective pore space. The

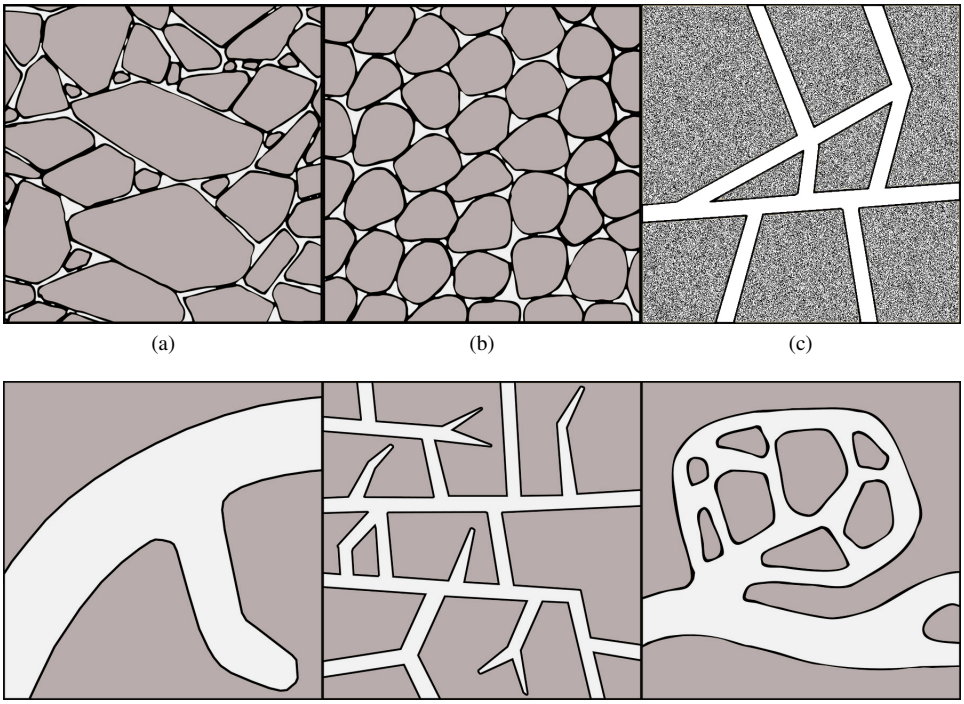

Figure 2.1: Examples of porous media: (a) - poorly sorted sedimentary rock with low porosity; (b) - well-sorted sand with high porosity; (c) - porous matrices separated by long fractures; (d) - dead pore channel; (e) - fractures with dead-ends; (f) - dead porous block.

distribution of the void space may form some dead-end pores or even areas where the fluid is completely stationary;

On Fig. 2.1 some most typical examples of porous systems are presented. Figures 2.1a and 2.1b are the well known sedimentary rocks originated from sand grains packed into a sandstone. Fig. 2.1c is a combination of porous matrices such as sandstones and larger fractures or cracks. Figures 2.1d–f demonstrate the appearance of dead pores and dead zones.

In the definition above we used a few important terms that require deeper explanation. Essential to the concept of a continuum is *the representative elementary volume* (REV) over which the average is performed. REV is the volume of the medium chosen small enough to represent the medium's characteristics but not taking into account the local fluctuations of the pore sizes or, in other words, not resolving the porous microgeometry.

An important and intuitive characteristic of a porous medium associated with REV is the medium's volumetric porosity. *Porosity* is usually defined as the ratio between the void space volume within REV and the total volume. Thus the definition of REV is constrained with the meaning of porosity. For a homogeneous porous medium REV must be large enough that the porosity is not affected by the micro-scale fluctuations.

In terms of a hetergeneous porous medium, porosity is varying in space, and the size of REV is the characteristic length indicating the rate at which the porosity changes.

Though the definition of the porous medium's porosity is intuitive, it should be considered more thoroughly. It is discussed above that due to the random nature of a medium some dead pores or even dead zones may appear. In these parts, the fluid does not move or moves slow enough that these dead zones do not participate in the average flow. In such case, we may define *the effective porosity* based on the flow profile and the distribution of the pore conductivities. It was reported by Vasilyev et al. [2012] that the presence of dead zones cannot be neglected and depends on the medium's topology.

When a fluid flows through a porous medium, it follows a number of paths through the medium's voids. Thus, it is reasonable to include another characteristic of the medium defined as the ration between the average path length traveled by the fluid and the length of the porous domain. This ratio is called the medium's *tortuosity* [Bear and Dagan, 1964, Carman, 1937]:

$$T = \left(\frac{L}{\langle L_s \rangle} \right)^2, \tag{2.1}$$

where L is the length of the flow domain and $\langle L_s \rangle$ is the average length of all possible flow paths. Tortuosity can also be defined in terms of its influence on the average velocity [Carman, 1937]:

$$T = \left(\frac{v}{\langle v_s \rangle} \right)^2, \tag{2.2}$$

where v is the large scale fluid velocity and $\langle v_s \rangle$ is the average of the mean velocities appearing in those paths.

The most important and the most useful, from a practical point of view, characteristic of a porous medium is *the hydraulic conductivity* which quantitatively describes the ability of the porous medium to transmit a specific fluid through it. Hydraulic conductivity relates the specific flux vector to the pressure gradient:

$$\mathbf{q} = -K \nabla \mathbf{p}. \tag{2.3}$$

Relation (2.3) is *the Darcy's law*, derived experimentally by Henry Darcy [Darcy, 1856]. The coefficient K depends on the porous medium's and the fluid properties and is usually obtained from experiments. Various attempts have been made to relate hydraulic conductivity to some properties of the porous matrix. An initial step can be made by splitting the parameters related to the medium's structure and the parameters related to the fluid as suggested by Nutting [1930]

$$K = \frac{kg}{\nu}, \tag{2.4}$$

where k is the permeability of the porous matrix, g is the gravity acceleration and ν is the dynamic viscosity of the fluid. Thus, the problem was reduced to parametrization of the porous matrix. For example, Krumbein and Monk [1943] suggested a purely empirical relation to the grain size:

$$k = 0.617 \times 10^{-11} d^2. \tag{2.5}$$

Fair and Hatch [1933], who based their approach on a dimensional analysis and experimental verifications, suggested:

$$k = \frac{1}{m}\left[\frac{(1-n)^2}{n^3}\left(0.01\alpha\sum\frac{P}{d_m}\right)^2\right]^{-1}, \tag{2.6}$$

where m is a packing factor, α is a grain shape coefficient, P is the porosity and d_m is the characteristic grain size.

In purely theoretical approaches to relate permeability to the medium's properties, the authors tried to resolve the micro-scale structure of porous matrices. They simplified the porous matrix with long capillary tubes [Scheidegger, 1953, Fatt, 1956] or a set of narrow capillary fissures [Irmay, 1955] or a bundle of capillary tubes of given shape and constant length [Carman, 1937]. With modern technologies, it became possible to improve these assessments by including the random nature: small scale heterogeneities and arbitrary channel shape. This led to a new direction in porous media studies: the pore network modeling.

2.2 Fine-scale numerical modeling of porous systems

When the early investigators tried to find the large scale parameters of porous media, they also understood the importance of linking these parameters to the medium's microgeometry [Carman, 1937, Wyllie and Spangler, 1952, Irmay, 1955, Scheidegger, 1953, Fatt, 1956, Scheidegger, 1960]. Hence, it was reasonable to address the fine-scale structure as well. Having limited computational opportunities, they had to work fully analytically by considering regular structures and averages. Growing computational capacity opened access to larger and more complex structures, shifting from regularity to randomization.

The idea of a fine-scale numerical representation of porous networks appeared together with the first attempts to obtain the parameters analytically. Carman [1937], Wyllie and Spangler [1952], Scheidegger [1953], Fatt [1956] have reasonably suggested that a porous medium can be interpreted as small interconnected capillaries. The technique of the pore-scale description of porous matrices is called *the pore-network modeling*, and it is widely used to describe macroscopic behavior by explicitly accounting for the physical phenomena on the pore scale. In order to reproduce the average phenomena, the models require an accurate description of the medium's morphology. It has been clearly demonstrated that the geometric properties, such as the distribution of the pore sizes and shapes, are crucial [Larson et al., 1977, 1991, Øren and S, 2003, Blunt et al., 1992, Heiba et al., 1992, Ioannidis and Chatzis, 1993, Pereira et al., 1996, Raoof and Hassanizadeh, 2010, Reeves and Celia, 1996, Dillard and Blunt, 2000]. It has also been shown that the network topology, such as connectivity, coordination number and coordination number distribution, plays a significant role in the mean process [Raoof and Hassanizadeh, 2010, Vasilyev et al., 2012].

It is common to consider a porous network as pore bodies interconnected with pore throats (Fig. 2.2). Obviously, the volume of both throats and bodies represents the void space of the porous medium which is one of the most important characteristics. Early attempts in pore-network modeling considered only regular networks, thus, omitting

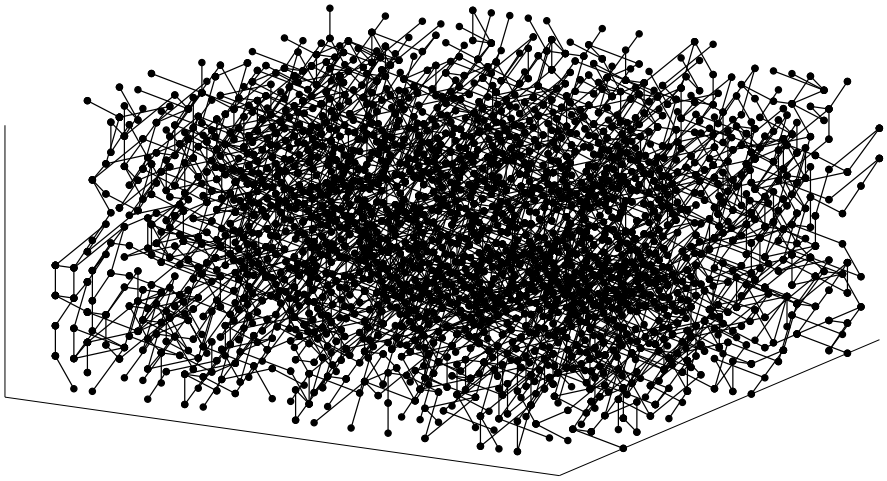

Figure 2.2: A pore-network model.

the network's random nature. At the same time, it has been discovered that equally or even more important is the network topology which is accounted by, for example, a number of connections to each pore body, called *the coordination number*, as well as the distribution of this number [Chatzis and Dullien, 1977, Wilkinson and Willemsen, 1983]. Accurate consideration of the network topology is crucial for proper description of the physical properties and mean transport quantification. Therefore, scientists employed various techniques for reconstruction of porous networks. Arns et al. [2004] compared different network topologies with the same mean coordination number and concluded that matching the coordination number distribution is crucial when generating the corresponding network models. Ioannidis et al. [1997], Bakke and Øren [1997], Øren et al. [1998] studied serial sections of a sandstone core and obtained *the mean coordination number* (CN) for those samples $CN = 3.5$–4.5. Flannery et al. [1987], Dunsmoir et al. [October 69 1991], Spanne et al. [1994] employed X-ray microtomography for direct resolution of 3D pore structures and found $CN = 4$ for the most sandstones. Lindquist et al. [2000] reported the coordination numbers of Fontainebleau sandstone up to 20, depending on the medium's porosity. Vasilyev et al. [2012] found that the coordination number can affect the average transport phenomena, that the networks with higher CN demonstrated more tailing in the BTCs as a result of non-Fickian behavior (the definition of non-Fickian transport will be discussed below).

Continuous development of pore network models reduced the need of laboratory experiments for obtaining the BTCs. Moreover, network models contain all necessary information about the medium which is, in contrast, very hard to obtain from a real sample. This information is of high importance for large scale models, as it can introduce relations to the model's parameter space.

In the next chapter, we give a brief introduction to Fickian and non-Fickian (anomalous) transport and focus on the usability of fine-scale models to demonstrate anomalous effects.

Chapter 3

Normal and anomalous transport in porous media

"No amount of experimentation can ever prove me right; a single experiment can prove me wrong."
–Albert Einstein

Understanding of physical phenomena underlying a process is crucial for setting up large scale models that are desired to be both accurate and physically consistent. Phenomenological relations are usually a good compromise for quantitative assessments as they are based on real observations. However, the phenomenon is, sometimes, too complex to be expressed with a simple equation and should be considered more thoroughly.

Fick's laws of diffusion are based on basic principles of molecules' heat motion and, therefore, can reasonably be applied to spreading of a plume in a flow domain. At the same time, the approach has failed in some cases, when it was applied to flow in porous media. In this chapter, we discuss the appearance of the "non-Fickian" transport phenomena in porous structures, but before we do that, we must, of course, discuss the original Fick's laws.

3.1 Fick's laws of diffusion

Molecules of any physical substance are always in random motion. This motion appears if the temperature of the substance is greater than 0^{o}K, and it is called *the heat motion of molecules*. In terms of fluid flow, this phenomenon forces particles to exchange, thus, resulting in a macroscale phenomenon called *diffusion*. Diffusion describes the spreading of particles due to their random movements from regions with higher concentrations to regions with lower concentrations. In other words, if a box contains molecules of red and blue color split by a wall, these molecules will fill the box uniformly at inifinite time after the wall has been removed (Fig. 3.1). This supports also the idea that any system should converge to an equilibrium state.

The way to quantify diffusion has first been introduced by Fick [1855], whose approach can be presented in his own words: "It was quite natural to suppose that this law for the diffusion of a salt in its solvent must be identical with that, according to which

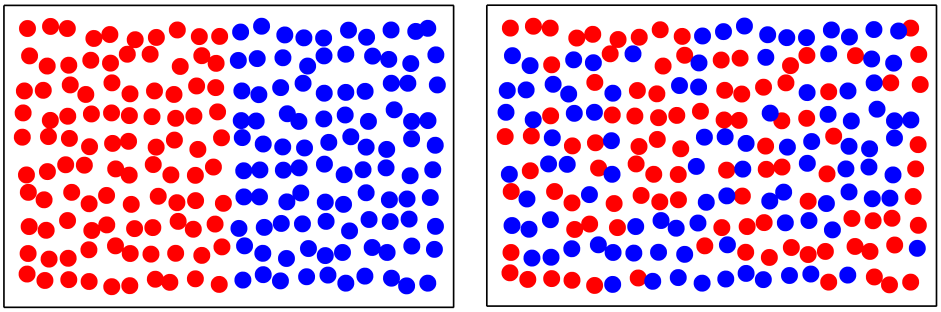

Figure 3.1: Effect of molecular diffusion.

the diffusion of heat in a conducting body takes place; upon this law Fourier founded his celebrated theory and it is the same which Ohm applied, with such extraordinary success, to the diffusion of electricity in a conductor".

Assume, that molecules can occupy only fixed points on a spatial lattice called sites with a probability to jump to the next site in any of the three dimensions $(\pm x, \pm y, \pm z)$. Let us define the frequency of such jumps ν, with the total amount of jumps over time given by νt. Such discrete approach refers to the random walk method that describes a path consisting of a consequence of random steps. If it was C molecules at a site initially, then it is possible to define the flux in, for example, $+x$ direction:

$$J_{+x}(x) = \frac{1}{6}\nu a C, \tag{3.1}$$

where a is the discretization length of the lattice. Accordingly, the number of molecules at the next site $x+\delta x$ is $C+\delta C$, and the flux in the opposite direction is defined as:

$$J_{-x}(x+\delta x) = \frac{1}{6}\nu a (C+\delta C). \tag{3.2}$$

Since δC is the change of concentration in x direction then

$$\delta C = a\frac{\partial C}{\partial x}. \tag{3.3}$$

Thus, the total flux can be expressed as:

$$J_{\text{net}} = -\frac{1}{6}\nu a^2 \frac{\partial C}{\partial x} = -D\frac{\partial C}{\partial x}. \tag{3.4}$$

Equation (3.4) is the Fick's first law of diffusion with the coefficient of proportionality D called *the diffusion coefficient* [Fick, 1855].

Fick's first law applies to steady state flux in a uniform concentration gradient. For a non-uniform case let us consider a part of the flow domain between x and $x+\delta x$. Flux in and out of the subdomain is defined as:

$$\begin{aligned} J_{\text{in}} &= -D\frac{\partial C}{\partial x}, \\ J_{\text{out}} &= J_{\text{in}} + \delta J = J_{\text{in}} + \delta x \frac{\partial^2 C}{\partial x^2}. \end{aligned} \tag{3.5}$$

Over the time interval δt the concentration changes by:

$$\delta C = \frac{J_{\text{in}} - J_{\text{out}}}{\delta x}\delta t. \tag{3.6}$$

And in case of constant diffusivity we obtain the Fick's second law

$$\frac{\partial C}{\partial t} = -\frac{\partial J}{\partial x} = D\frac{\partial^2 C}{\partial x^2}. \tag{3.7}$$

Description of the molecule jumps above leads to an important statement that the average displacement is defined as:

$$\bar{x} = a\sqrt{\nu t} \cong \sqrt{Dt}, \tag{3.8}$$

which refers to Gaussian distribution. Therefore, such behavior is often referred as normal, Gaussian or Fickian, in contrast to anomalous, non-Gaussian or non-Fickian, when the displacement distribution is not Gaussian.

In the next chapter, we discuss the application of Fick's ideas to porous flow and present the non-Fickian behaviour in porous systems.

3.2 Non-Fickian dispersion in homogeneous porous networks

In Chapter 2.2, we mentioned pore network models for numerical fine scale resolution of transport phenomena. A porous network is the synthetic representation of a porous and fractured medium. Pore throats or fractures are typically represented as tubes of various shapes serving for flow phenomenon, whereas pore bodies are volumes that accumulate the fluid and serve for fluid mixing. Pore network modeling is a powerful tool which allows to simulate processes in homogeneous and heterogeneous porous media, multi-permeable systems and many others.

Flow spreading in a porous network can be described in terms of molecular diffusion: particles occupy discrete sites and have their frequency of displacements. In a realistic porous network the pore conductivities are random which leads to random frequency for each kind of a random walk (site-to-site displacement). The central limit theorem assures that on average all these random displacements converge to Gaussian distribution. Therefore, it is reasonable to make a hypothesis that dispersion in porous media should satisfy the Fick's laws [Kitanidis, 2017]. Thus, the average fluid transport in a homogeneous porous medium can be described with the *Advection-Dispersion Equation* (ADE)

$$\frac{\partial c}{\partial t} + \nabla \cdot (\bar{u}c - D\nabla c) = 0. \tag{3.9}$$

c is the medium's saturation or fluid concentration, $\bar{u}$ is the mean fluid velocity and D is the dispersion coefficient accounting for spreading of the concentration profile.

The effect of fluid dispersion resembles the molecular diffusion. Indeed, both phenomena are caused by a distribution of particle velocities. In terms of diffusion, this is the Maxwell-Boltzmann distribution of molecular speeds, while the distribution of the pore network properties, such as pore channel conductivities, leads to dispersion.

Another separately standing phenomenon of Taylor dispersion should also be mentioned in this section. Taylor dispersion is the effect of the flow profile spreading in small capillary tubes due to friction on the walls [Taylor, 1953]. Wall friction acts on the fluid layers creating a parabolic velocity profile across the tube. On average, the quantitative impact of Taylor dispersion is described as an addition to the diffusion coefficient. Thus, the effective dispersion coefficient D in (3.9) should be a composition:

$$D_{\text{eff}} = \text{Diffusion} + \text{Taylor dispersion} + \text{network dispersion}.$$

ADE is often referred as the advection-diffusion equation, when only molecular diffusion is considered. In order to avoid any confusion, we would like to emphasize that both names refer to the same equation, where the coefficient D is denoted for different phenomena. Before and after, we use the term "advection-dispersion equation" for ADE in order to point out its universality.

Though ADE and its variants are widely used also nowadays, deviations has been reported in both numerical and natural experiments while fitting ADE to breakthrough curves (BTCs) [Aronofsky and Heller, 1957, Scheidegger, 1959, Vasilyev et al., 2012, Kitanidis, 2017]. It has been demonstrated in laboratory experiments that dispersion is scale-dependent [Silliman and Simpson, 1987] in contrast to the fundamental assumption that the disperisivity is only a function of the porous medium's microgeometry. Such scale-dependent behavior is referred as *non-Fickian, non-Gaussian or anomalous*.

The problem of ADE's applicability arises from our understanding of "homogeneity". In a real porous medium, heterogeneities are present at all scales. This requires a better knowledge of the medium which cannot be summarized in a single constant and thus, needs more sophisticated models.

One example of such scale-dependent behavior has been presented in Vasilyev et al. [2012], where the disperisivity of virtually homogeneous porous networks was investigated with the respect to the mean network coordination number explained below. In Raoof and Hassanizadeh [2010] it was suggested to compose a synthetic porous structure such that the pore throats are interconnected by the pore bodies located on a regular cubic lattice. The number of pore throats connecting in a pore body, called *the coordination number*, was randomized by removing arbitrarily some of the pore throats. The resulting coordination number distribution was log-normal with *the mean network coordination number* introduced as one of the main parameters describing the porous network. Investigating the networks with the mean network coordination number varying from 3 to 15, it was finally concluded that the networks with higher coordination numbers have demonstrated higher anomality of the BTCs. This anomality appeared as "long tails", and it is commonly known as *the tailing effect*. One of the reasons for the tailing effect in homogeneous porous networks is the appearance of dead zones - parts of the network where the fluid moves very slowly [Yang et al., 2016]. This is more probable in the networks with high mean network coordination number, therefore, a more complicated structure.

Many authors have striven to improve the quality of transport quantification as well as the description of the underlying processes. The first and the most logical attention has been directed towards ADE and its dispersion coefficient which has been reintroduced as a function of time, concentration or flow velocity [Hundsdorfer and Verwer, 2013, Sanskrityayn and Kumar, 2016]. It has later been criticized, that the governing

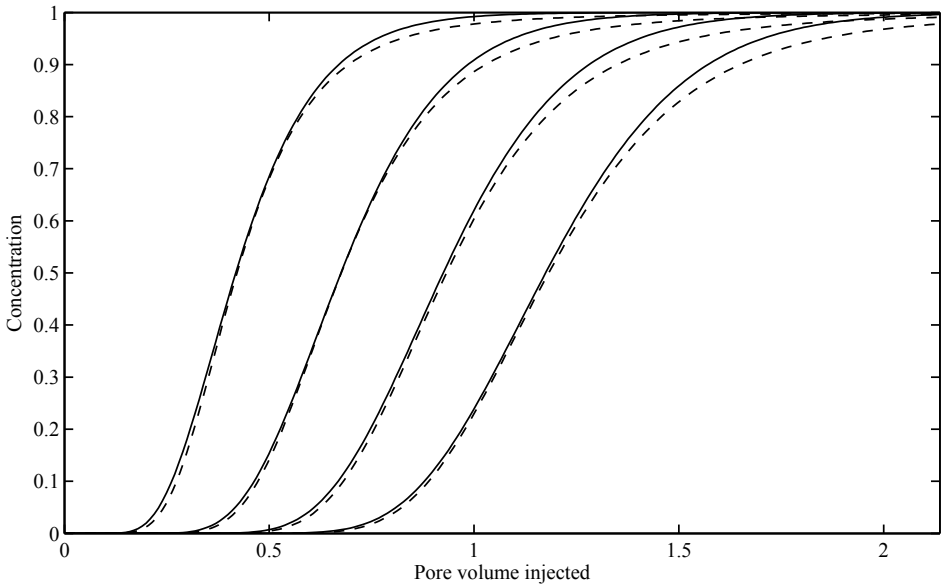

Figure 3.2: Long tails appearing in the BTCs from the pore network simulation (dashes). Solid lines represent the fitted solution of ADE.

equations are deterministic which required that the physical quantities were defined on a representative elementary volume large enough to render their space-time variations slow enough. In a anomalous regime the variables change so rapidly that they should be treated as random functions of space and time over a macroscopic continuum, which leads to a stochastic approach.

In the next chapter we present some of the most known and used large scale models for transport in porous materials and focus our attention to the recently introduced Generalized Continuum Transport (GCT) model.

Chapter 4

Large scale models for transport in porous media

"Divide each difficulty into as many parts as is feasible and necessary to resolve it."
–Rene Descartes

Despite that porous systems are often treated as homogeneous at some scale, they are essentially multiscale heterogeneous, and therefore, cannot be described with certainty at all scales and locations of relevance. Alternative approaches address the scale and space-time dependencies in different ways.

Some of the methods describe transport at some reference scale with the classical ADE where velocity is a spatially correlated random field. The approach refers to variations of pore conductivities and leads to the stochastic ADE. Averaging the stochastic ADE over the ensemble of the velocity fields results in a space and time non-local representation of the mean advective-dispersive flux. Representation of the advective-dispersive flux that is non-local in time but local in space leads to the Continuous Time Random Walk model (CRTW) and the Multirate Mass Transfer model (MRMT). A form of ADE entailing fractional derivatives yields a representation of advective-dispersive flux which is local in time but non-local in space. Stochastic approaches are attractive for numerical simulations as they do not introduce numerical diffusion into the scheme.

The main difficulty in the large-scale quantification of transport phenomena arises from the selection of a model and the corresponding parameter space which is often made a priory. For the models mentioned above, the form of the parameter space is crucial for the most accurate results. Constraining the parameters space and providing the physical interpretations of the modeling choice are the main challenges in the applicability of the generalized models. In order to address these problems, the Generalized Continuum Transport model (GCT) has been introduced.

In this chapter, we provide an overview of the existing classical and generalized transport models and introduce the Generalized Continuum Transport model as the ultimate solution for model selection and parameter estimation.

4.1 The classical advection-dispersion equation

The macroscopic description of tracer propagation in a uniform medium by means of ADE is based on the Fick's laws (Chapter 3.1), from which it follows that a macroscopic mass flux $\mathbf{J}(\mathbf{x},t)$ at any point $\mathbf{x}$ of the continuum at time t can be expressed as:

$$\mathbf{J} = \mathbf{J}_{\text{adv}} + \mathbf{J}_{\text{diff}} + \mathbf{J}_{\text{disp}}, \tag{4.1}$$

where $\mathbf{J}_{\text{adv}}$ is the advective mass flux related to the mean fluid velocity $\mathbf{v}(\mathbf{x},t)$, $\mathbf{J}_{\text{diff}}$ represents the effect of molecular diffusion across the channel and $\mathbf{J}_{\text{disp}}$ is the dispersive mass flux due to random deviations of the fluid velocities from their macroscopic average $\mathbf{v}$. It follows, that the fluxes are related to the concentration of contaminant as:

$$\mathbf{J}_{\text{adv}} = \mathbf{v}c, \quad \mathbf{J}_{\text{diff}} = -D_{\text{mol}}\nabla c, \quad \mathbf{J}_{\text{disp}} = -\mathbf{D}_{\text{disp}}\nabla c. \tag{4.2}$$

Fick's second law provides, that the solute mass is conserved on a macro-scale. Assuming that there are no sources or sinks in the medium, we obtain:

$$\frac{\partial c}{\partial t} = -\nabla \cdot \mathbf{J}. \tag{4.3}$$

Substituting (4.2) into (4.3) we derive the advection-dispersion equation:

$$\frac{\partial c}{\partial t} = -\nabla \cdot (\mathbf{v}c) + \nabla \cdot (\mathbf{D}_{\text{eff}}\nabla c), \tag{4.4}$$

where $\mathbf{D}_{\text{eff}} = D_{\text{mol}}\mathbf{I} + \mathbf{D}_{\text{disp}}$ is the effective dispersion coefficient, and $\mathbf{I}$ is the identity matrix.

Though, it was reported by many authors that ADE is inadequate to quantify non-Fickian behavior [Aronofsky and Heller, 1957, Scheidegger, 1959, Silliman and Simpson, 1987], it is still widely used in many applications due to its simplicity and possibility to obtain the parameters from laboratory experiments.

In the next chapters, we present some of the most well known approaches to treat anomalous phenomena in porous flow and introduce a new model, called *Generalized Continuum Transport* (GCT).

4.2 Stochastic advection-dispersion equation

The problem of ADE to accurately describe non-Fickian transport arises from its deterministic nature which requires that all physical quantities entering the equation are defined on a representative elementary volume (REV) large enough to represent their space and time variations sufficiently slow. For real porous media it is more common to consider the parameters on smaller support volumes (related here and below as ω), since averages can be unreliable in a system with large fluctuations. Physical quantities defined on the scale of ω vary so rapidly, that they should be treated as random functions of space and(or) time over a macroscopic continuum. Thus, ADE becomes stochastic.

Let us consider contaminant propagation as a cloud of particles, where each particle makes a series of space transitions before the velocity $\mathbf{v}$ changes. In the deterministic

approaches, the velocity $\mathbf{v}$ and the dispersion $\mathbf{D}$ are defined in each REV as an average. The stochastic approaches are based on the assumption that Fickian behavior occurs on the local support scale ω, thus, can be described by the classical ADE. Let us now start with the following equation:

$$\frac{\partial c}{\partial t} = -\nabla \cdot (\mathbf{v}c) + \nabla \cdot (\mathbf{D}_l \nabla c) + g, \tag{4.5}$$

subject to initial and boundary conditions:

$$c(\mathbf{x}, t=0) = C_0(\mathbf{x}), \mathbf{x} \in \Omega, \tag{4.6a}$$
$$c(\mathbf{x}, t) = C_D(\mathbf{x}, t), \mathbf{x} \in \Gamma_1, \tag{4.6b}$$
$$-\mathbf{D}_l \nabla c(\mathbf{x}, t) \cdot \mathbf{n}(\mathbf{x}) = W(\mathbf{x}, t), \mathbf{x} \in \Gamma_2, \tag{4.6c}$$
$$[\mathbf{v}(\mathbf{x}, t)c(\mathbf{x}, t) - \mathbf{D}_l \nabla c(\mathbf{x}, t)] \cdot \mathbf{n}(\mathbf{x}) = P(\mathbf{x}, t), \mathbf{x} \in \Gamma_3. \tag{4.6d}$$

(4.6a) is the initial condition on a flow domain Ω. (4.6b) sets the random concentration C_D on the boundary segment Γ_1. (4.6c) describes the random dispersive flux W normal to the boundary segment Γ_2. (4.6d) determines the random advective-dispersive flux normal to the boundary segment Γ_3.

Assume, that the local dispersion coefficient $\mathbf{D}_l$ in (4.5) is constant and deterministic, while the velocity $\mathbf{v}$ is a space-time non-stationary random field satisfying a stochastic flow equation:

$$\nabla \mathbf{v} = f_\omega(\mathbf{x}, t), \tag{4.7}$$

where $f(\mathbf{x}, t)$ is an ω scale random fluid source. Introduce a term g accounting for a presence of random sources. Hence, $\mathbf{v}$, c and g are random functions, that can be split into their averages and disturbances:

$$\begin{aligned} \mathbf{v}(\mathbf{x}, t) &= \langle \mathbf{v}(\mathbf{x}, t) \rangle_c + \mathbf{v}'(\mathbf{x}, t), \\ c(\mathbf{x}, t) &= \langle c(\mathbf{x}, t) \rangle_c + c'(\mathbf{x}, t), \\ g(\mathbf{x}, t) &= \langle g(\mathbf{x}, t) \rangle_c + g'(\mathbf{x}, t), \end{aligned} \tag{4.8}$$

where $\langle \cdot \rangle$ denotes the conditional ensemble's mean, and the primed quantities are the zero-mean random fluctuations. Decomposing all random functions in (4.5), we obtain:

$$\frac{\partial \langle c \rangle_c}{\partial t} = -\nabla \cdot (\langle \mathbf{v} \rangle_c \langle c \rangle_c) + \nabla \cdot (\mathbf{D}_l \nabla \langle c \rangle_c + \mathbf{Q}_c) + \langle g \rangle_c, \mathbf{x} \in \Omega, \tag{4.9}$$

where $\mathbf{Q}_c(\mathbf{x}, t) = \langle \mathbf{v}'(\mathbf{x}, t) c'(\mathbf{x}, t) \rangle_c$ is the conditional dispersive flux. (4.9) is subject to initial and boundary conditions analogues to (4.6):

$$\langle c(\mathbf{x}, t=0) \rangle_c = \langle C_0(\mathbf{x}) \rangle, \mathbf{x} \in \Omega, \tag{4.10a}$$
$$\langle c(\mathbf{x}, t) \rangle_c = \langle C_D(\mathbf{x}, t) \rangle, \mathbf{x} \in \Gamma_1, \tag{4.10b}$$
$$-\mathbf{D}_l \nabla \langle c(\mathbf{x}, t) \rangle_c \cdot \mathbf{n}(\mathbf{x}) = \langle W(\mathbf{x}, t) \rangle, \mathbf{x} \in \Gamma_2, \tag{4.10c}$$
$$[\langle \mathbf{v}(\mathbf{x}, t) \rangle_c \langle c(\mathbf{x}, t) \rangle_c - \mathbf{D}_l \nabla \langle c(\mathbf{x}, t) \rangle_c + \mathbf{Q}_c(\mathbf{x}, t)] \cdot \mathbf{n}(\mathbf{x}) = \langle P(\mathbf{x}, t) \rangle, \mathbf{x} \in \Gamma_3. \tag{4.10d}$$

In a bounded domain, $\mathbf{Q}_c$ is given exactly by the implicit relation [Morales-Casique

et al., 2006]:

$$\begin{aligned}
\mathbf{Q}_c(\mathbf{x},t) = &\int_0^t \int_\Omega \langle G(\mathbf{x},t;\mathbf{y},\tau)\mathbf{v}'(\mathbf{x},t)\rangle_c \nabla_\mathbf{y}\cdot\mathbf{Q}_c(\mathbf{x},t;\mathbf{y},\tau)d\mathbf{y}d\tau \\
&- \int_0^t \int_\Omega \langle G(\mathbf{x},t;\mathbf{y},\tau)\mathbf{v}'(\mathbf{x},t)\mathbf{v}'^T(\mathbf{y},\tau)\rangle_c \nabla_\mathbf{y}\langle c(\mathbf{y},\tau)\rangle_c d\mathbf{y}d\tau \\
&- \int_0^t \int_\Omega \langle G(\mathbf{x},t;\mathbf{y},\tau)\mathbf{v}'(\mathbf{x},t)f'(\mathbf{y},\tau)\rangle_c \langle c(\mathbf{y},\tau)\rangle_c d\mathbf{y}d\tau \\
&- \int_0^t \int_{\Gamma_3} \langle G(\mathbf{x},t;\mathbf{y},\tau)\mathbf{v}'(\mathbf{x},t)\rangle_c \nabla_\mathbf{y}\cdot\mathbf{Q}_c^T(\mathbf{x},t;\mathbf{y},\tau)\mathbf{n}(\mathbf{y})d\mathbf{y}d\tau \\
&+ \int_0^t \int_{\Gamma_3} \langle G(\mathbf{x},t;\mathbf{y},\tau)\mathbf{v}'(\mathbf{x},t)\mathbf{v}'^T(\mathbf{y},\tau)\rangle_c \langle c(\mathbf{y},\tau)\rangle_c \mathbf{n}(\mathbf{y})d\mathbf{y}d\tau,
\end{aligned} \tag{4.11}$$

where $G(\mathbf{x},t;\mathbf{y},\tau)$ is the random Green's function satisfying a stochastic ADE with homogeneous (zero) initial and boundary conditions [Morales-Casique et al., 2006]. Since G depends on the boundary configuration but not on the boundary values, the same yields $\mathbf{Q}_c$ as long as the initial-boundary values are independent of $\mathbf{v}$. The terms in (4.11) form non-local parameters which depend on the flow field but not on the transport-related forcing terms.

An important advantage of the model is that the only modeling assumption to be made is the validity of ADE on the local scale of measurement ω. Such generality provides the establishment of the space-time non-locality in a compact mathematical form. The model represents the mean behavior as a result of the spatio-temporal dependencies (including correlations) between the velocity fluctuations and, as follows, between the randomly heterogeneous parameters (permeability and porosity) that control it.

However, (4.9) to (4.11) do not provide a closed form system. The kernels of (4.11) contain unknown moments which evaluation requires additional assumptions or approximations. If the velocity $\mathbf{v}$ is space-time stationary, the ensemble moments of the Green function depend only on space and time increments, i.e $G(\mathbf{x}-\mathbf{y},t-\tau)$, and the first and the fourth terms in (4.11) can be dropped. In order to produce a stationary velocity field, the flow domain must be infinite such that the boundary integrals of (4.11) vanish. The remaining integrals turn into space-time convolutions and the mean transport equation becomes:

$$\begin{aligned}
\frac{\partial\langle c\rangle_c}{\partial t} = -\nabla\cdot\Bigg(\Bigg[&-\langle v\rangle\langle v\rangle + \int_0^t\int_\Omega \langle G(\mathbf{x}-\mathbf{y},t-\tau)\mathbf{v}'(\mathbf{x},t)\mathbf{v}'^T(\mathbf{y},\tau)\rangle\nabla_\mathbf{y}\langle c(\mathbf{y},\tau)\rangle d\mathbf{y}d\tau \\
&+ \int_0^t\int_\Omega \langle G(\mathbf{x}-\mathbf{y},t-\tau)\mathbf{v}'(\mathbf{x},t)f'(\mathbf{y},\tau)\rangle\langle c(\mathbf{y},\tau)\rangle d\mathbf{y}d\tau + \mathbf{D}_l\nabla\langle c\rangle\Bigg] + \langle g\rangle.
\end{aligned} \tag{4.12}$$

The subscript c has been omitted because conditioning would require the velocity field to be non-stationary. Stationarity implies the mean advective velocity $\langle v \rangle$ be constant, the flow domain has to be infinite, free of sources, and no data conditioning is possible. This limits significantly the functionality of the model.

Stochastic ADE is based on the classical ADE formulation. Let us now focus on a probabilistic approach presented in the next chapter.

4.3 Continuous Time Random Walk

The idea of the random walk models rests on a representation of fluid flow, where fluid particles (molecules or small volumes) occupy discrete sites of the flow domain. Particles residing at a site $\mathbf{s}$ leave to a site $\mathbf{s}'$ with a transition rate $w(\mathbf{s}',\mathbf{s})$ which determines the number of transitions per unit time. At the same time, the particles residing at $\mathbf{s}'$ arrive at $\mathbf{s}$ with a transition rate $w(\mathbf{s},\mathbf{s}')$. Denoting the bulk particle concentration as $c(\mathbf{s},t)$, we can find the concentration change by appealing to the mass conservation principles:

$$\frac{\partial c(\mathbf{s},t)}{\partial t} = -\sum_{\mathbf{s}'} w(\mathbf{s}',\mathbf{s})c(\mathbf{s},t) + \sum_{\mathbf{s}'} w(\mathbf{s},\mathbf{s}')c(\mathbf{s}',t). \tag{4.13}$$

The above equation is known as *the Master Equation* [Oppenheim et al., 1977, Shlesinger, 1996]. The transition rates describe the effect of the velocity field on the particle motion and represent the detailed knowledge of the system. The Master Equation does not distinguish the effects of varying velocity field into advective and dispersive terms.

Definition of $w(\mathbf{s},\mathbf{s}')$ requires a complete description of the system. Thus, the heterogeneities must be characterized on all length scales influencing the flow field. Therefore, a distribution of w on the subdomain should be addressed. To realize the probabilistic approach, let us consider the ensemble average of (4.13), which has the form of *the Generalized Master Equation* (GME) [Klafter and Silbey, 1980]:

$$\begin{aligned}\frac{\partial P(\mathbf{s},t)}{\partial t} = &-\sum_{\mathbf{s}'}\int_0^t \phi(\mathbf{s}'-\mathbf{s},t-t')\langle c(\mathbf{s},t')\rangle dt' \\ &+\sum_{\mathbf{s}'}\int_0^t \phi(\mathbf{s}-\mathbf{s}',t-t')\langle c(\mathbf{s}',t')\rangle dt',\end{aligned} \tag{4.14}$$

where $P(\mathbf{s},t)$ is the average concentration. In contrast to (4.13), GME is non-local in time, since it contains integration over time accounting for the past state of the concentration. The ensemble average of (4.13) for a heterogeneous system leads to a non-local equation, because the role of the transition rates w is replaced by a distribution of transit times $\phi(\mathbf{s}'-\mathbf{s},t-t')$ between sites. Thus, the transition rates are time-dependent but stationary, depending only on the difference $(\mathbf{s}'-\mathbf{s})$, which represents the available information about the system on a certain scale.

In the context of the Continuous Time Random Walk Model (CTRW), the bulk concentration is replaced by the probability per time for a particle to just arrive at site $\mathbf{s}$

at time t:

$$R(\mathbf{s},t) = \sum_{\mathbf{s}'} \int_0^t \psi(\mathbf{s}-\mathbf{s}', t-t') R(\mathbf{s}', t') dt', \tag{4.15}$$

where $\psi(\mathbf{s},t)$ is the probability per time for a displacement $\mathbf{s}$ with a difference of arrival times t. It has been proved that CTRW is completely equivalent to GME with the correspondence [Kenkre et al., 1973, Shlesinger, 1974]:

$$P(\mathbf{s},t) = \int_0^t \left(1 - \int_0^{t-t'} \psi(\tau)\, d\tau\right) R(\mathbf{s},t')\, dt', \tag{4.16a}$$

$$\mathcal{L}(\phi(\mathbf{s},u)) = \frac{u\mathcal{L}(\psi(\mathbf{s},u))}{1-\mathcal{L}(\psi(u))}, \tag{4.16b}$$

where $\mathcal{L}$ denotes Laplace transformation (it is important to mentioned that the CTRW model is often considered in Laplace space). $\psi(t)$ is the probability of a particle to leave the site at time t:

$$\psi(t) = \sum_{\mathbf{s}} \psi(\mathbf{s},t). \tag{4.17}$$

Let us consider a simple example of a one-dimensional random walk: the particles start initially from the same point, and each particle jumps after a given period of time either to the left $(-\Delta x)$ or to the right $(+\Delta x)$ with equal probability. After conducting n such steps, the particles may appear at any of the points: $-n\Delta x, -(n-1)\Delta x, ..., -\Delta x, 0, \Delta x, ..., (n-1)\Delta x, n\Delta x$. Assuming that the displacements are all independent, the probability of any sequence of n steps is 0.5^n. Accordingly, the probability of a particle to arrive at a point $m\Delta x$ after n displacements is:

$$p(m,n) = \frac{n!}{\left(\frac{n+m}{2}\right)!\left(\frac{n-m}{2}\right)!} \cdot 0.5^n. \tag{4.18}$$

(4.18) is the *Bernoulli distribution*, which variance or, in other words, the root mean square displacement is exactly $\sqrt{n}$. When n is sufficiently large and $m \ll n$, the distribution limits to a continuous form as the normal distribution:

$$p(m,n) = \sqrt{\left(\frac{2}{\pi n}\right)} e^{-m^2/2n}. \tag{4.19}$$

Substituting $x = n\Delta x$ and assuming that a particle makes u displacements per unit time Δt, we obtain:

$$p(x,t) = \sqrt{\frac{1}{4\pi D t}} e^{-x^2/4Dt}, \tag{4.20}$$

where $D = u\Delta x^2/2$. Thus, this simple statistical transport model is equivalent to ADE with the mean displacement $\bar{x}(t)$ proportional to time and standard deviation $\sigma(t)$ proportional to the square root of time, as shown in Chapter 3.1:

$$\begin{aligned} \bar{x}(t) &\sim t, \\ \sigma(t) &\sim \sqrt{t}. \end{aligned} \tag{4.21}$$

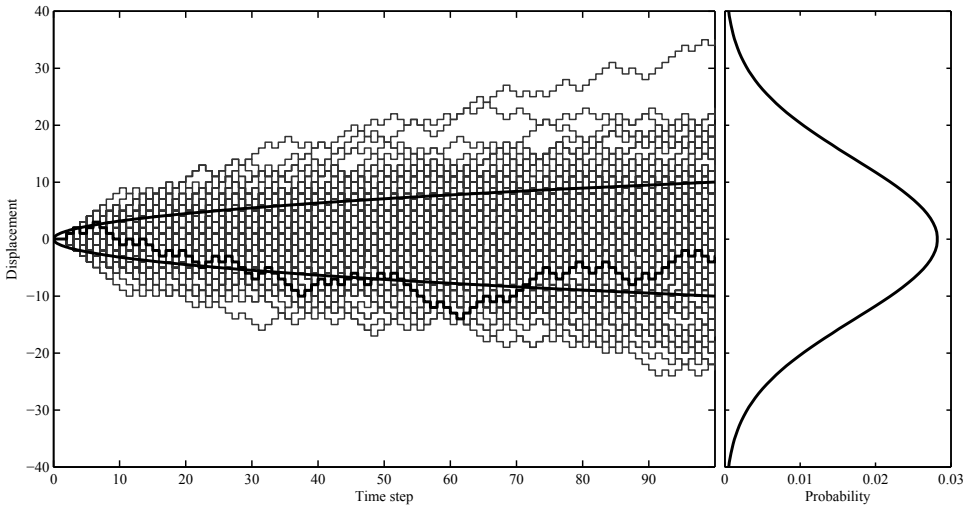

Figure 4.1: Illustration of the random walk approach. 200 particles start from the same point, performing one step upwards or downwards with equal probability. The cloud of particles spreads out with each time step. Theoretical particle density distribution after 100 walks (time steps) is plotted on the right axes.

Figure 4.1 illustrates the behavior of 200 random walkers started from the same initial point. After each time step, the cloud of particles spreads out demonstrating Fickian-type transport.

A similar but more substantial approach is presented as the Global Random Walk by Suciu et al. [2011], Suciu [2014], who replaced the mean velocity in ADE with a random velocity fields. These models are very attractive in terms of numerical analysis which assumes discretization but do not introduce numerical diffusion in the scheme [Radu et al., 2011].

The probability of displacements introduced as $\psi(\mathbf{s},t)$ in CTRW accounts for the transport nature. For the basic example discussed above, $\psi(\mathbf{s},t)$ becomes simply:

$$\psi(\mathbf{s},t) = \begin{cases} 0.5, & s = \pm\Delta x, t = \Delta t, \\ 0, & \text{elsewhere.} \end{cases} \tag{4.22}$$

In realistic highly disordered media, the variation of rates (values of $w(\mathbf{s},\mathbf{s}')$) determined by the flow field is very large, and the temporal distribution dominates the transport nature. The temporal aspects of particle transport is the key feature of the CTRW approach, giving rise to anomalous effects. Therefore, definition of $\psi(\mathbf{s},t)$ is the key to a proper model set up and accurate quantification.

CTRW is often considered on an ordered site lattice using an average rate, that $w(\mathbf{s},\mathbf{s}')) = w(\mathbf{s}-\mathbf{s}'))$, and $\psi(\mathbf{s},t)$ varies slowly in time as a power law:

$$\psi(\mathbf{s},t) \sim t^{-1-\beta}, \tag{4.23}$$

which accounts for a wide distribution of event times in a highly disordered medium. It has been shown that the power law behavior refers to non-Fickian transport [Scher and

Montroll, 1975, Berkowitz and Scher, 2001]. In this case, $\psi(\mathbf{s},t)$ can be decomposed into the spatial and temporal dependencies such that $\psi(t)$ has also the power law. Thus, β is the effective parameter accounting for the behavior of transitions over a time period corresponding to the duration of observation. The form of $\psi(t)$ at large time determines the time dependence of the mean displacement $\bar{x}(t)$ and the standard deviation $\sigma(t)$ of $R(\mathbf{s},t)$. It has been shown by Scher and Montroll [1975], Shlesinger [1974] that under a constant pressure gradient for $0 < \beta < 1$:

$$\begin{aligned} \bar{x}(t) &\sim t^{\beta}, \\ \sigma(t) &\sim t^{\beta}, \end{aligned} \tag{4.24}$$

whereas for $1 < \beta < 2$:

$$\begin{aligned} \bar{x}(t) &\sim t, \\ \sigma(t) &\sim t^{(3-\beta)/2}, \end{aligned} \tag{4.25}$$

which is in stark contrast to Fickian behavior (4.21). Dentz and Berkowitz [2003] has shown that $\beta > 2$ refers to normal transport behavior

The CTRW approach has been utilized by many authors who reported excellent results of fitting the breakthrough curves obtained both from numerical and natural experiments [Berkowitz et al., 2000, Levy and Berkowitz, 2003, Berkowitz et al., 2006, Bijeljic and Blunt, 2006, Boano et al., 2007, Cortis et al., 2006]. It has been shown that CTRW has limits to ADE [Berkowitz and Scher, 2001], stationary stochastic ADE [Neuman and Tartakovsky, 2009] and can take a form of a fractional differential equation (FDEs are discussed below) [Berkowitz et al., 2002]. However, the functionality of the CTRW approach is limited by the definition of the transition time $\psi(t)$ which does not account for any porous medium characteristic. The selection of the form of $\psi(t)$ is made intuitively, and the parameters of the distribution are further guessed or fitted. Another critical point arises from the discrete nature of the CTRW model which was originally applied for electrons occupying discrete energy levels but is less suitable for a continuous fluid flow.

Nevertheless, CTRW is an interesting framework that motivated further development of probabilistic approaches considered in the next chapter.

4.4 Special forms of CTRW: multi-rate mass transfer, factional derivative ADE

In Chapters 2.2 and 3.2, we discussed the appearance of dead zones in a random porous system, where the fluid velocity is relatively small. This phenomenon is addressed directly in a multi-rate mass transfer (MRMT) formulation which distinguishes mobile and immobile solute fractions [Pfister and Scher, 1978, Haggerty and Gorelick, 1995]. Though the approach is often discussed in a context of heterogeneous or highly disordered medium, we would like to emphasize that slow motion areas appear also in random but homogeneous media as demonstrated by Vasilyev et al. [2012].

In MRMT the total solute concentration is decomposed into mobile and immobile phase such that:

$$c(\mathbf{s},t) = c_{\mathrm{m}}(\mathbf{s},t) + c_{\mathrm{im}}(\mathbf{s},t), \tag{4.26}$$

and the change of concentration is governed by advective and diffusive flux of the mobile phase:

$$\frac{\partial c(\mathbf{s},t)}{\partial t} = -\mathbf{v}\cdot\nabla c_{\mathrm{m}}(\mathbf{s},t) + \nabla\cdot\mathbf{D}\nabla c_{\mathrm{m}}(\mathbf{s},t). \tag{4.27}$$

(4.27) must be enclosed by a linear relation between the mobile and the immobile concentrations accounting for the transitions between phases. The relation can, for example, be introduced as a multiple trapping process, which involves first-order transitions into and out of the immobile phase. Thus, we can write:

$$\begin{aligned} \frac{\partial c_{\mathrm{im}}(\mathbf{s},t)_i}{\partial t} &= c_{\mathrm{m}}(\mathbf{s},t)\omega_i - c_{\mathrm{im}}(\mathbf{s},t)_i W_i, \\ c_{\mathrm{im}}(\mathbf{s},t) &= \sum_i c_{\mathrm{im}}(\mathbf{s},t)_i, \end{aligned} \tag{4.28}$$

where ω_i is the trapping rate and W_i is the release rate of the i-th trap level. The traps are characterized by their level (energy) independent of their position in space. It has been shown that this model is a subset of CTRW [Schmidlin, 1977, Pfister and Scher, 1978]. Solving (4.27) together with (4.28) in Laplace space, it is possible to obtain the transition rate [Berkowitz et al., 2006]:

$$\mathcal{L}(\psi(u)) = \left[1 + u\bar{t} + u\bar{t}\sum_i \frac{\omega_i}{u+W_i}\right]^{-1}, \tag{4.29}$$

where $\bar{t} = \left(\sum_i \omega_i\right)^{-1}$ is the average time spent in the mobile state (between two traps). Thus, the random walk is a series of transitions in the mobile phase between traps.

(4.28) can be generalized in a continuous form $W_i \to t_r$ with a distribution of levels $P(t_r)$ and a transfer function $R(t/t_r)$ [Carrera et al., 1998, Haggerty et al., 2000, Dentz and Berkowitz, 2003]:

$$c_{\mathrm{im}}(\mathbf{s},t) = \int_0^\infty P(t_r)\omega(t_r)\,dt_r \int_0^t R((t-t')/t_r)c_{\mathrm{m}}(\mathbf{s},t')\,dt'. \tag{4.30}$$

The forms of the transfer function $R(t/t_r)$ and the trapping rate $\omega(t_r)$ are determined by the mass exchange mechanism between the mobile and the immobile phases.

Past years, more attention has been paid towards the fractional derivative (FDE) form of CTRW also known as the fractional ADE (fADE) [Metzler et al., 1998, Meerschaert et al., 1999, Hilfer, 2000, Metzler and Klafter, 2000]. The idea of derivatives having fractional order has been postulated by Leibniz and L'Hopital who naturally suggested that:

$$d^{1/2} \sim x\sqrt{\frac{dx}{x}}$$

as a generalization of

$$\frac{d^n}{dx^n}x^k = \frac{k!}{(k-n)!}k^{k-n}$$

for non-integer orders:

$$\frac{d^\alpha}{dx^\alpha}x^k = \frac{\Gamma(k+1)}{\Gamma(k-a+1)}k^{k-n}.$$

There exist several definitions for fractional operators, however, at this point, it is enough to focus on the two of them applicable for transport formulation: the Riemann-Louville fractional time derivative:

$$D^{\alpha} f(t) = \frac{d^m}{dx^m} \left[\frac{1}{\Gamma(m-\alpha)} \int_0^t \frac{f(\tau)}{(t-\tau)^{\alpha-m+1}} dt \right], m \in \mathbb{N}, m-1 < \alpha \leq m, \tag{4.31}$$

and the Riesz spatial derivative [Oldham and Spanier, 1974, Samko et al., 1993].

Time-FDE follows directly from the case when the transition time has the power law (4.23) with the parameter $0 < \beta < 1$, for which the temporal moments are infinite. The Riemann-Liouville fractional integral has the form:

$$\frac{\partial^{-\beta}}{\partial t^{-\beta}} P(\mathbf{s},t) := \frac{1}{\Gamma(\beta)} \int_0^t \frac{P(\mathbf{s},t')}{(t-t')^{1-\beta}} dt, \tag{4.32}$$

which possesses an important property:

$$\mathcal{L} \left\{ \frac{\partial^{-\beta}}{\partial t^{-\beta}} P(\mathbf{s},t) \right\} = u^{-\beta} \widetilde{P}(\mathbf{s},u). \tag{4.33}$$

The negative index of (4.32) refers to fractional differentiation. It has been shown that time-FDE yields the fractional order ADE [Compte, 1997, Compte et al., 1997, Compte and Ca'ceres, 1998, Metzler et al., 1998, Metzler and Klafter, 2000]:

$$\frac{\partial}{\partial t} P(\mathbf{s},t) = \frac{\partial^{1-\beta}}{\partial t^{1-\beta}} \left(-\mathbf{v}_{\beta} \cdot \nabla + K_{\beta} \nabla^2 \right) P(\mathbf{s},t), \tag{4.34}$$

where $\mathbf{v}_{\beta}$ is the "generalized drift velocity" and K is the anomalous dispersion constant. Thus, the probability density $P(\mathbf{s},t)$ described by the time-fractional ADE is equivalent to the large time limit of CTRW with an asymptotic form of transition times defined as the power law (4.23).

The opposite case of the transition time distribution, with an existing first moment appearing when $\beta > 1$, refers to a random displacement between discrete sites, where time is not involved, called a Lévy flight. Analogously as for the time-FDE, let us apply the power law for the transition length:

$$P(\mathbf{s},t) \sim |\mathbf{s}|^{-1-\mu}, \; 0 < \mu < 2, \tag{4.35}$$

The Riesz operator ∇^{μ} is defined in Fourier space as [Samko et al., 1993]:

$$\mathcal{F}\{\nabla^{\mu} P(\mathbf{s},t)\} = -|\mathbf{k}|^{\mu} \mathcal{P}(\mathbf{k},t), \tag{4.36}$$

with the characteristic function

$$\mathcal{P}(\mathbf{k},t) = \exp(-K^{\mu})t|\mathbf{k}|^{\mu}. \tag{4.37}$$

Thus for an assymptotic form of $P(\mathbf{s},t)$ the Lévy flight fractional ADE takes a form [Metzler et al., 1998]:

$$\frac{\partial}{\partial t} P(\mathbf{s},t) + \mathbf{v} \cdot \nabla P(\mathbf{s},t) = K^{\mu} \nabla^{\mu} P(\mathbf{s},t). \tag{4.38}$$

Both forms of FDE represent generalizations of the Fickian ADE and are special cases of CTRW. These formulations have limited applicability due to the diverging first or second moment which are usually used to determine the drift velocity and the dispersion coefficient.

4.5 Dual and multiple continua models

In Chapter 4.4, we discussed the MRMT approach to splitting the medium into two continua: one mobile and one immobile, which corresponds directly to the processes in a random porous system as presented in Chapter 2.2. Another example of a dual-continuum medium is a combination of similar porous blocks separated by larger fractures. Such system is treated as homogeneous on a large scale but a heterogeneous dual-continuum nature should be taken into account for proper modeling. This corresponds also to the idea that in a real porous media the fluid follows preferential paths. Flow media consisting of two ore more continua have traditionally been modeled using dual- or multiple-porosity models [Barenblatt et al., 1960, Edwards et al., 1979, Hoogmoed and Bouma, 1980, Berkowitz et al., 1988, Gerke and Genuchten, 1993].

A typical dual-porosity model is based on a simple ADE formulation assuming Fickian, non-compressible flow in each continuum:

$$\begin{aligned} \varphi_p \frac{\partial c_p}{\partial t} &= -\nabla \cdot (\mathbf{v}_p c_p - \mathbf{D}_p \nabla c_p) - N_p f, \\ \varphi_f \frac{\partial c_f}{\partial t} &= -\nabla \cdot \left(\mathbf{v}_f c_f - \mathbf{D}_f \nabla c_f\right) - N_f p, \end{aligned} \tag{4.39}$$

where indices p and f refer to the porous matrix continuum and the fractured continuum correspondingly. φ is the weighting factor defined by the volume ratio:

$$\varphi_\omega = V_{\text{omega}}/V_{\text{total}},\ \omega \in \{p, f\}. \tag{4.40}$$

The terms $N_p f$ and $N_f p$ account for the mass transfer between the two continua. Mass conservation requires that:

$$N_p f = -N_f p, \tag{4.41}$$

as the species leaving one continuum should immediately enter the other continuum. It is common to assume, that the mass transfer term is proportional to the concentration difference between the pore-matrix and the fractured continua:

$$N = n(c_p - c_f). \tag{4.42}$$

Generalizing the concept of the dual-porosity model with application to multiple-continuum media, it is natural to rewrite the multiple-porosity model in a form:

$$\varphi_\omega \frac{\partial c_\omega}{\partial t} = -\nabla \cdot (\mathbf{v}_\omega c_\omega - \mathbf{D}_\omega \nabla c_\omega) - \sum_{\xi \in \Omega} N_{\omega,\xi},\ \omega \in \Omega. \tag{4.43}$$

Same as before, $N_{\omega,\xi}$ accounts for the mass exchange between the two continua, and it is proportional to the concentration difference. Ω denotes a set of porous continua, where each element corresponds to the volume, where the fluid moves with a given velocity.

It is interesting that in general, there is no restriction on the drift velocity in each continuum. This means that one of the continuum may have zero velocity, accounting for the the dead zones. Vasilyev et al. [2012] have demonstrated the importance of the dead zones and included the immobile continuum in their simulations [Vasilyev et al., 2017].

The major focus for authors investigating the applicability of the multiple-continuum model has become the mass exchange and its dependence on the medium's characteristics.

Following the discussion above that in a real porous system "heterogeneities" are present at all scales and the scales are a continuous set, it is logical to extrapolate the idea of the multiple-continuum models on a continuous scale. This refers to a new approach presented in Chapter 4.6.

4.6 Generalized Continuum Transport model

The main purpose of the transport models is the representation of flow phenomena in porous media on a large scale without resolving the microstructure of a medium. The effect of fluid propagation is usually observed by measuring fluid saturation or concentration at a few control points. The result of this observation is called the breakthrough curve (BCT), which is the concentration change in time at a certain point. Mimicking those BTCs by a transport model is the quantification of the phenomena. Model accuracy can further be qualified by comparing the BTCs obtained from an experiment (numerical or laboratory) and the BTCs of the considered model. On the other hand, the BTCs can be used for finding the model parameters, such as velocity and dispersion coefficients of ADE or transition time distribution of CTRW.

Let us see, for example, how the BTCs on Fig. 3.2 can be quantified with ADE. Consider a case of a 1D semi-infinite homogeneous porous domain unsaturated initially with a constant saturation source on the boundary. This means that the porous domain is thin enough that it can be treated as 1D, and long enough to omit the boundary effects of the sink side. This domain is initially filled with fresh water (unsaturated fluid) and salt water (saturated fluid) is injected from the source side at a constant rate. Fluid inside the domain moves with a drift velocity v_x and the effect of transversal spreading is captured by the dispersion coefficient D. ADE corresponding to such system has a form of:

$$\frac{\partial c}{\partial t} + \mathbf{v_x}\frac{\partial c}{\partial x} - D\frac{\partial^2 c}{\partial x^2} = 0, \tag{4.44}$$

where $c(x,t)$ is the saturation or, in this particular case, the normalized salt water concentration. The solution of (4.44) for the given conditions is known to be:

$$c(x,t) = \operatorname{erfc}\left(\frac{x - \overline{v_x}t}{\sqrt{2Dt}}\right), \tag{4.45}$$

where $\operatorname{erfc}(x)$ is the cumulative error function defined as

$$\operatorname{erfc}(x) = \frac{2}{\sqrt{\pi}}\int_x^\infty e^{-\zeta^2} d\zeta. \tag{4.46}$$

The parameters v_x and D can be found by matching the experimental BCTs with the solution of ADE. As seen on Fig. 3.2, ADE cannot properly quantify the BTCs as they originate from the porous network with highly non-Fickian flow.

Aiming to accurately quantify the BTCs obtained from an experiment or network models, a researcher must pick up a transport model and estimate model parameters. After the model has been selected, the parameters can be found from different sources such as guessing, curve fitting or fluid (density, viscosity) and medium's characteristics (some porous media characteristics have been discussed in Chapter 2.1). However, the model selection is not parametrized and the choice should be made a priory based on the researcher's knowledge and experience. Therefore, a proper model selection is crucial for appropriate description of the transport mechanisms and good predictions.

The CTRW approach has resolved the problem of modeling choice, at least partially, by introducing the power law for anomalous transport. The power law parameters determine the transport regime and in limit cases refer to Fickian behavior. However, the usage of the power law is also a subject for discussion as well as the applicability of CTRW for a continuous process. Parameters of the CTRW model are usually guessed or fitted, thus require obtaining the breakthrough curves.

Multiple-porosity models rely on the information about the velocity field, which, in principle, can be related to the medium's characteristics [Wang and Narasimhan, 1985, Gerke and Genuchten, 1993, Vasilyev et al., 2017]. The number of the governing partial differential equations in the system (4.43) controls the model complexity which can be adjusted to the desired accuracy of simulations. Each equation indexed by ω corresponds to the porous volume, where the fluid moves with the given velocity. Thus, v is the velocity distribution within the porous medium. But can a multiple porosity model limit to CTRW and other existing models?

In a real porous medium heterogeneities are present at all scales and preferential flow is significant. Thus, the velocity distribution of (4.43) should, in general, be continuous, accounting for all possible velocity variations. Can we rewrite the multiple porosity model on a continuous scale?

These issues are addressed in the Generalized Continuum Transport model introduced in Nordbotten and Vasilyev [2010], Vasilyev et al. [2017]. This model is designed in order to satisfy the four key requirements:

1. the equations are formulated at a continuum scale large enough that the porous structure is not resolved;
2. the model is capable to accurately quantify anomalous transport:
3. the model has existing models as certain limits:
4. the model is based on continuous, local transport of particles in space-time.

These requirements are partially met by the classical models, but in GCT they are all satisfied as a solid set.

Let us generalize Ω in (4.43) to be a space of properties, denoted for each physical point $\mathbf{x}$ at a continuum scale. Ω can be varying on the subscale relevant to the transport mechanisms involved. Ω is multi-dimensional accounting for the correlation of mineral distributions with velocities or pore radii. In certain limits, it can be a space of sub-scale velocities or fluxes, and in discrete form it refers to the classical

	φ	v	ω
Transport equation	$\{1\}$	$\{v\}$	$\{1\}$
Dual porosity model	$\{\varphi_1, 1-\varphi_1\}$	$\{v_1, v_2\}$	$\{1,2\}$
ADE	$\mathbb{R}^1$	$\mathbb{R}^1$-Gaussian	$\mathbb{R}^1$
Multiple Continua	finite set	finite set	finite set
CTRW	$\mathbb{R}^1$-distribution	$\mathbb{R}^1$-distribution	$\mathbb{P}\times\mathbb{R}^+$
MRMT	$\mathbb{R}^2$-distribution	$\mathbb{R}^2$-distribution	$\mathbb{P}^2\times\mathbb{R}^+$ function of trapping time

Table 4.1: GCT limits to classical models. Table from Vasilyev et al. [2017]

models. If the physical properties are varying in time, then Ω must also be denoted for a time domain. Concentration of a contaminant c is a function of $(\mathbf{x},t,\omega)$, where $(\mathbf{x},t,\omega)\in X\times T\times\Omega$, and X and T are space and time domains correspondingly. According to the requirements specified above, transport is modeled in the spatial domain as continuous, corresponding to the standard conservation equation with a linear and local flux expression. The above assumptions lead to an equation for contaminant concentration in (X,T,Ω) space:

$$\phi\varphi\frac{\partial}{\partial t}c+\nabla\cdot\mathbf{j}=N(c|_{\mathbf{x},t},\omega). \tag{4.47}$$

It is important that the interaction functional $N(c|_{\mathbf{x},t},\omega)$ acts only on c as a function of ω and, in general, depends on the transport properties of the medium. The void space distribution φ is, in general, a function of $(\mathbf{x},t,\omega)$, while the porosity ϕ is a constant determined by the porous medium. Thus, the void space distribution must satisfy:

$$\int\limits_{\omega\in\Omega}\varphi(\mathbf{x},t,\omega)d\omega=1,\forall(\mathbf{x},t)\in X\times T. \tag{4.48}$$

The fluid flux $\mathbf{j}$ is generally a function of $(c,\mathbf{x},t,\omega)$. The mass conservation implies the first moment of the interaction functional to be zero:

$$\int\limits_{\omega\in\Omega}N(c|_{\mathbf{x},t},\omega)d\omega=0. \tag{4.49}$$

Construction of the parameter space $(X\times T\times\Omega)$ accounts for various physical phenomena and refers to different transport models. The choice of Ω is crucial for accurate and physically reasonable transport description. It has been demonstrated that the parameter space of GCT has flexible nature, such that it can be transformed matching the transport phenomena which nature remains unknown [Vasilyev et al., 2017]. This is in stark contrast with the classical principles when the modeling choice has to be done and the parameter space has to be constrained.

Let us consider some examples of the parameter space Ω and the models it can lead to (Table 4.1). The most obvious form of the interaction functional occurs when the mass exchange rate is directly proportional to the concentration gradient. Following (4.42), we obtain:

$$N(c|_{\mathbf{x},t},\omega)=\int\limits_{\xi\in\Omega}n(\omega,\xi)dc_\omega(\xi), \tag{4.50}$$

where $n(\omega,\xi)$ is a scalar mass transfer coefficient. If Ω is discrete, denoting the species moving with the same velocity, then GCT limits directly to the multiple porosity model (4.43). If Ω consists of only two elements, then GCT takes the form of the dual porosity model (4.39).

GCT limit to the basic ADE with constant coefficients is not so straightforward and can be obtained by a proper introduction of coefficients $(v_\omega,\varphi_\omega)$, which represent and can be determined from an accounting velocity distribution. Some examples of the velocity distributions obtained from Fickian type transport models have been shown in Vasilyev and Radu [2017a]. However, the problem of a continuous distribution, which leads to ADE, remains unresolved.

In Nordbotten and Vasilyev [2010] a limit to CTRW has been derived. The mass transfer term has been obtained in a form of Bhatnagar-Gross-Krook collision operator [Bhatnagar et al., 1954], which corresponds to the mass per time entering collisions or, in other words, mass per time leaving a continuum:

$$N_i(c|_{\mathbf{x},t}) = \langle m_i/\tau\rangle_i f_{i,\text{coll}} - m_i/\tau, \tag{4.51}$$

where f_{coll} is the mass distributed from the collisions:

$$f_{i,\text{coll}}(\tau) = \frac{f_{i,\text{eq}}(\tau)/\tau}{\langle f_{i,\text{eq}}(\tau)/\tau\rangle_i}, \tag{4.52}$$

and f_{eq} is the equilibrium mass distribution. The characteristic time-scale of relaxation τ has been included in order to present the time scale of collisions into the parameter space that $\Omega = \mathcal{P}\times\mathcal{R}^+$. Treating the governing equations in a Lagrangian form, the similarity between GCT and CTRW has been derived, where

$$f_{i,\text{coll}}(\tau) = \psi_{\text{CTRW}}(\mathbf{x}_i,\tau), \tag{4.53a}$$

$$f_{i,\text{eq}} \sim \tau\psi_{\text{CTRW}}(\mathbf{x}_i,\tau). \tag{4.53b}$$

GCT limit to MRMT can be easily obtained by following the same procedure applying two mass transfer distributions: one for mobile phase and another one for immobile.

It has, therefore, been shown that the model selection can be parameterized by introducing the space Ω into the GCT model. It has also been demonstrated that the modeling choice can also be governed by a set of parameters, i.e. scalars or distributions. The model can be adjusted to the desired accuracy and complexity directly during the calculations.

The benefits of the GCT model can be summarized in a few points:

- equations are formulated on a continuous space;
- model complexity can be directly determined and parametrized;
- the parameter space can be adjusted to a desired complexity and accuracy;
- model parameters are directly related to physical characteristics of a medium;

- model parameters can be directly determined from fine-scale modeling of transport phenomena.

Let us explain the nature of GCT in the following simple way. Consider a cloud of particles (or fluid molecules) entering a porous matrix. Each particle has its own velocity, but for the complete particle cloud a velocity distribution can be assigned according to natural properties of the fluid, as, for example, Gaussian distribution due to heat motion in Chapter 3.1. Traveling through the manifold of pore channels and junctions, each particle follows a path of its own length and arrives at a observation point of its own time. Thus, an average drift velocity can be associated with each particle. This approach is also reflected in the multiple-porosity models, where a finite set of drift velocities is associated with the particle cloud. In reality, the amount of molecules is so high, that it is hard to address each one separately and the velocity set becomes a continuous distribution. Moreover, there always exist particles that will never arrive at the observation point being stuck in the dead zones. On the other hand, heat motion provides particles with infinitely high velocities. This means that an average model should take all possible velocities into account as a continuous distribution, as done in GCT.

Similar discussion can also be applied for the distribution of the porous medium's properties. In a real porous medium, all pore conductivities can be found, though the probability to meet extremely small as well as extremely high conductivities is infinitely small. The same applies the pore connectivities as discussed in Chapter 2.2, where the mean network coordination number was declared equally important as its distribution. In other words, the mean pore connectivity (or coordination number) varies continuously from 0 to the designed network maximum. Thus, the medium's porosity and the mass transfer function are also continuous distributions.

We can also employ the idea of preferential flow in a real porous medium. Larger amount of particles will follow a certain path through pores and junctions, while other particles will choose different ways. Considering all possible paths on a continuous scale, it is possible to refer to a distribution of paths, where weight related to the void space distribution is associated with each path.

4.7 Numerical solution of GCT

Though a continuous parameter distribution is the key to GCT, for numerical purposes the equations should be discretized. Hence, it is more practical to consider GCT in a form of the multiple porosity model with the linear interaction term:

$$\phi\varphi_\omega\frac{\partial c_\omega}{\partial t}+\nabla\cdot(\mathbf{v}_\omega c_\omega)=\sum_{\xi\in\Omega}n(\omega,\xi)(c(\omega)-c(\xi)),\ \text{for each}\ \omega\in\Omega. \tag{4.54}$$

In (4.54), the unknowns are the continuum fractions φ_ω, the velocities v_ω and the mass exchange rates $n(\omega,\xi)$. When the porous medium's properties are not specified, the most reasonable way to find the parameters of the GCT model is the curve fitting. Thus, transport through the porous medium is modeled either numerically or naturally, and the BTCs are fitted with a solution of GCT. Fitting means guessing the parameters such that the BCTs of the experiment and the model are as close to each other as possible.

Proximity of the curves can be assessed visually, but it is more accurate to estimate the proximity error as, for example:

$$err = \sum_{x \in X_p} \int_0^t \sqrt{c_{\text{model}}(x,\tau)^2 - c_{\text{exp}}(x,\tau)^2}, \tag{4.55}$$

where X_p is a set of observation points. Minimization of the error in the form of (4.55) is called *the least squares method*, which is widely used for relatively smooth data sets.

So, the best parameter set is obtained, when the proximity error is lowest, but how the parameters are guessed and found? We suggest using the Nelder-Mead optimization method [Nelder and Mead, 1965] for finding a minimum of a multivariate function which is the error in the considered case. This method belongs to a general class of derivative-free methods, so called, *direct search methods*, which are advantageous, when a system of partial differential equations is to be solved. Parameters of the multivariate function (φ_ω,v_ω,$n(\omega,\xi)$) are variated based on an initial guess and a set of procedures.

1. Initial simplex - Construct an initial simplex by generating vertices $x_1, x_1, \ldots x_{N+1}$ around an initial point $x_{in} \in \mathbb{R}^N$. In our case x_{in} is composed from all parameters of GCT taking into account that $n(\omega,\xi) = n(\xi,\omega)$ according to (4.49). It is typical, that all edges have the same specific length.

2. Ordering - Order the initial simplex from the lowest calculated proximity error to the highest. After ordering, the worst point x_{N+1} is discarded and a new point is calculated.

3. Centroid - Calculate the centroid of the best side by discarding the worst point:

$$x_c = \frac{1}{N} \sum_{i \neq N+1} x_i.$$

4. Reflection - Reflect away from the worst point

$$x_r = x_c + \alpha(x_c - x_w).$$

   If the proximity error at this point is lower than that at the second worst point but larger than that at the best point $err(x_1) < err(x_r) < err(x_N)$, then accept the new point. Otherwise, proceed to contraction.

5. Expansion - If the proximity error of the reflected point is lower than that at the best point $err(x_r) < err(x_0)$, then calculate an expansion point

$$x_e = x_c + \gamma(x_r - x_c).$$

   If the new point is better: $err(x_e) < err(x_r)$, then accept it, otherwise accept the result of the reflection in the new simplex.

6. Contraction - Perform contraction between x_c and the best of the two points x_r and x_{N+1}:

$$x_s = x_c + \beta(x_r - x_c), err(x_N) \leq err(x_r) < err(x_{N+1})$$

$$x_s = x_c + \beta(x_{N+1} - x_c), err(x_r) > err(x_{N+1})$$

   If the contracted point is better, then it is accepted. Otherwise, shrinking is performed.

7. Shrinkage - Compute N new vertexes:

$$x_i = x_1 + \delta(x_i - x_1).$$

8. Iterate.

The algorithm iterates until a preset small variation of the parameters does not reduce the proximity error. The algorithm parameters are $\alpha > 0$, $0 < \beta < 1$, $\gamma > 1$, $\gamma > \alpha$, $0 < \delta < 1$, which are called reflection, expansion, contraction and shrinkage respectively. The process is highly dependent on the original guess and can, in some cases, converge to a local minimum, which provides unreliable results. Therefore, it is useful to perform minimization of the fitting error for a few initial points or even start the process again on the previous guess. If the algorithm struggles to find a better point, it can reflect the point to a completely different region, where a better minimum will be found. Implementations of the algorithm can easily be accessed in many programming languages as *fminsearch* in Matlab or *commons-math* in Java.

For a given set of parameters, GCT can be solved numerically using, for example, the finite difference method. For a discussion on the numerical diffusion in the related discretization schemes, we refer to Radu et al. [2011]. The equation (4.54) is rewritten in a form:

$$\begin{aligned}\varphi(\omega)\frac{c_k^n(\omega) - c_k^{n-1}(\omega)}{\Delta t} = &- \varphi(\omega)\overline{u}(\omega)\frac{c_k^n(\omega) - c_{k-1}^n(\omega)}{\Delta x} + \\ &+ \sum_{\xi \in \Omega} n(\omega,\xi)(c_k^n(\omega) - c_k^n(\xi)),\end{aligned} \tag{4.56}$$

applied initial conditions (non-saturated domain):

$$\forall \omega \in \Omega, \quad c(x, t = 0, \omega) = 0, \quad x \in X, \tag{4.57}$$

and boundary conditions (full saturation at the inlet):

$$\forall \omega \in \Omega, \quad c(x = 0, t, \omega) = 1, \quad t \in T. \tag{4.58}$$

The average concentration $\overline{c}(x,t)$ is calculated from the weighted sum:

$$\overline{c}(x,t) = \sum_{\omega \in \Omega} \varphi(\omega) c(\omega). \tag{4.59}$$

Since GCT in the discrete form (when Ω is a finite set) transforms into the multiple continua model (4.54), (4.56) is simply a system of algebraic equations that can easily be solved.

Chapter 5

Summary of results and conclusions

"Success is a science; if you have the conditions, you get the result."
–Oscar Wilde

In this chapter we provide an overview of the scientific results presented in the included papers.

The main objective of our research is to introduce the new Generalized Transport model as a robust tool for transport quantification and analysis of phenomena occurring when a fluid flows through a porous medium. This is done by linking GCT to some useful existing transport models through certain limits, finding the model parameters and comparing against the conventional approaches.

Paper B should be mentioned separately as it provides a method for fine-scale transport modeling, which is used in order to demonstrate the appearance of non-Fikcian behavior in homogeneous synthetic porous networks and to provide the BTCs for further fitting. At the same time, network characteristics provide parameters for the GCT model.

5.1 Summary of paper A: On the Relationship Between Multiple Porosity Models and Continuous Time Random Walk

Generalized Continuum Transport model was first suggested in Paper A as a replacement for the Continuous Time Random Walk approach. The purpose was to provide a more reliable model, continuous in both space and time and accurate in terms of anomalous transport quantification. Consequently, the authors realized that GCT is not just another transport model but a new framework that encloses the existing gaps in modeling choice and estimation of model parameters.

Applicability of the space-discrete CTRW model for the continuous phenomenon has been argued even by the authors of the model [Berkowitz et al., 2006, Dentz and Berkowitz, 2003]. Nevertheless, the model has widely been used due to its accuracy and availability of the numerical schemes. In Paper A, the new GCT model is introduced and its relation to CTRW is found. The nature of GCT is studied in terms of a simple example, where the parameters of GCT are obtained from a regular 2D porous network, but through the parameters of CTRW.

This study inspired further investigations of the GCT framework focusing on the selection of the parameter space, relations to the classical models and estimation of the model parameters from the fine scale simulations of porous flow.

5.2 Summary of paper B: Effect of Mean Network Coordination Number on Dispersivity Characteristics

Non-Fickian transport behavior was initially observed in a set of experiments as systematic deviations that could not be explained by the classical principles [Aronofsky and Heller, 1957, Scheidegger, 1959]. Berkowitz et al. [2006] have postulated that the effect appears in all realistic porous media due to their natural "inhomogeneity" - heterogeneities that are present on all scales. This statement doubts our understanding of a homogeneous porous system and REV. In Paper B, fluid flow through a realistic porous network is considered by studying the network dispersivity dependence on the network topology. A side result of this study was a discovery of anomalous transport effects in the porous networks with large coordination numbers, even though the networks have been constructed virtually "homogeneous", but randomized in order to match the real porous media.

Pore-network modeling is a numerical reconstruction of a real porous system in order to perform transport simulations on a computer instead of laboratory testing. Paper B is based on the previous approach for construction of realistic synthetic pore-network models, and transport equations are included in order to obtain the BTCs. The main focus is the pore network characteristic, called *the network coordination number*, which is the number of pore throats connecting to a single pore body. In terms of a large porous network, it is useful to consider the mean network coordination number and a distribution of these numbers. The distribution is usually fixed according to a realistic distribution of coordination numbers in porous systems, while the mean coordination number can vary depending on the type of the medium to be reconstructed.

Dispersion in a porous network accounts for spreading of the concentration profile and can appear on smaller and larger scales. On the pore scale, the spreading is caused by the heat motion of molecules (diffusion) and friction on capillary walls (Taylor dispersion), as discussed in Chapter 3.1. On a larger scale, spreading occurs due to the network structure or topology (geometrical dispersion [Bear, 1972]). The overall spreading is a combination of all phenomena with the effective dispersion coefficient of the form:

$$D^* = D_{\mathrm{m}} T + \alpha_G v + \alpha_T v^2, \tag{5.1}$$

where D_{m} is the molecular diffusion coefficient, T is the medium's tortuosity, α_G is the geometrical dispersivity, α_T is the Taylor dispersivity coefficient and v is the mean velocity.

In the study, transport equations are added and the geometrical dispersivity of the network is calculated from the second moment of the BTCs. It is found that geometrical dispersivity is correlated with the mean network coordination number and an empirical relation is proposed:

$$\alpha_G(\bar{z}) = \alpha_0 + c \times \exp^{-\delta(\bar{z}-2)}, \tag{5.2}$$

where α_0 is the geometric dispersivity at the highest mean network coordination number, $\bar{z}$ is the mean network coordination number and c, δ are some constants.

It was also pointed out that systematic deviations in the BTCs, which is the effect of anomalous transport, grow with the mean network coordination. It is especially important for deeper investigations of non-Fickian phenomena in homogeneous but random porous networks, which construction, topology and characteristics are know and can be related to the model parameters.

5.3 Summary of paper C: On the Properties of the Parameter Space of the Generalized Continuum Transport Model for Description of Fluid Flow in Porous Networks

Investigation of the GCT model continued in Paper C, but now more attention was paid to the nature of the parameter space and the relation to the medium's characteristics. From that point GCT, is primarily considered in its discretized form which leads to the multiple continua limit.

In Paper C we focused also on the construction of the parameter space of GCT. It is proposed that the benefit of the model is not the accurate prediction of flow, but an opportunity to constrain the parameter space, or, in other words, to parametrize the modeling choice.

The realistic network models from Paper B are used as a source of the BTCs, as well as the medium with known characteristics. Consequently, the parameter space is determined from the velocity distribution in the network and the desired accuracy of transport quantification is linked to the construction of the parameter space. It is emphasized that the parameter space can be determined based on the network properties and accuracy not only prior to modeling but also "on-the-fly", during the solution of GCT, thus taking into account the transport complexity at the moment.

Consider the following example: transport in a porous network is to be modeled with the discrete form of GCT. First, the velocity distribution should be obtained. This can be done by the fine-scale modeling of the porous network. For the velocity distribution, it is sufficient to calculate only the pressure at the network nodes and suggest some uniform network properties. A typical velocity distribution is shown on Fig. 5.1. It is remarkable how many nearly-zero velocities appear in a realistic medium which is exactly the influence of the dead zones. Discretized form of GCT is a system of differential equations with interactions:

$$\begin{cases} \phi\varphi_0 \frac{\partial c_0}{\partial t} + \mathbf{v}_0 \frac{\partial c_0}{\partial x} = \sum_i n(0,i)(c(0) - c(i)), \\ \phi\varphi_1 \frac{\partial c_1}{\partial t} + \mathbf{v}_1 \frac{\partial c_1}{\partial x} = \sum_i n(1,i)(c(1) - c(i)), \\ \vdots \\ \phi\varphi_N \frac{\partial c_N}{\partial t} + \mathbf{v}_N \frac{\partial c_N}{\partial x} = \sum_i n(N,i)(c(N) - c(i)). \end{cases} \tag{5.3}$$

It is important that in order to account for the zero-velocity term one equation in (5.3) should have the velocity equal to (e.g. $v_0 = 0$). After the model is initialized, we can follow three directions:

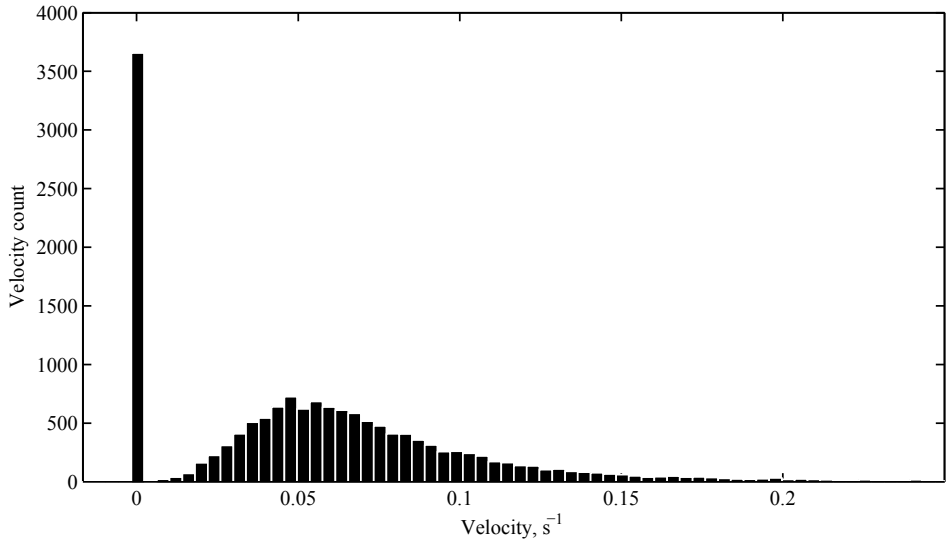

Figure 5.1: Velocity distribution in a regular porous network with the mean coordination number equal to 15. Figure from Vasilyev et al. [2017]

1. **Static adaption to the medium's structure.** This assumes that the medium consists of several subdomains with different complexity, for example a porous matrix and fractures (as on Fig. 5.2). The porous matrix has more complex structure and requires higher order of GCT for accurate quantification (Vasilyev et al. [2017] advise setting N>5 for accurate prediction of anomalous transport), while fractures can be modeled with fewer equations which saves computational efforts.

2. **Automatic adaption to the medium's structure.** If the structure of the multidomain medium is initially unknown, it is reasonable to apply initially higher order of GCT for each subdomain. After the simulation is started, it is possible to judge the flow complexity and reduce the order if necessary. Transport complexity can be verified by, for example, evaluating the distance between the concentration profiles in a pair of continua:

$$\varepsilon = |c_i(x,\tau) - c_j(x,\tau)|_{L2}$$

   at a predefined time point τ.

3. **Dynamic adaption to transport complexity.** Same as above, if the transport complexity (or desired accuracy) is initially unknown, it is possible to start with a larger number of equations. The complexity can be judged at each time step and the order can be reduced if necessary and increased back, when needed. This can be especially useful to model passing of a plume. For better performance, the order of GCT can be increased in the region where the plume is passing, and reduced on a subdomain, where concentration is not changing.

The examples above demonstrate how the modeling choice can be constrained and the configuration of the parameter space can be related to the medium's and transport properties.

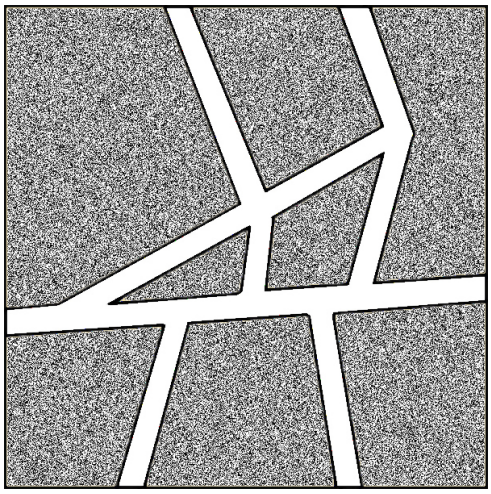

Figure 5.2: Heterogeneous porous medium consisting of homogeneous porous blocks and fractures.

5.4 Summary of paper D: Applying Some Natural Velocity Distributions for the Generalized Continuum Transport Model

It is emphasized in Chapter 4.6 that the equations entering the GCT model do not contain the second order spatial derivative which accounts for spreading of the concentration profile. It is suggested that ommition of this term does not limit the functionality of the model, but it is more natural to have parameter distribution accounting for spreading. Moreover, the lack of the second order derivative highlights the principles of GTC, where transport phenomena are represented as distributions over a continuous scale. In this case, dispersion on a large scale is accounted by the velocity distribution.

The main focus of Paper D is to show, that though the dispersion or the second order term is not included in GCT, it can model ADE by accounting for the Fickian-type velocity distribution. Moreover, the parameters of GCT are directly related to the velocity distribution in the medium. Contaminant flow through a long circular channel is considered in order to obtain the BTCs, which can be accurately approximated by ADE, and the dispersion coefficient can be estimated. Taylor dispersion [Taylor, 1953] due to wall friction dominates in the fluid domain, thus known flow nature provided the velocity distribution for the GCT model. It is demonstrated that GCT represents spreading of the concentration profile by accounting for the corresponding velocity distribution. Hence, GCT models physical phenomena in a more natural way by appealing to the actual flow characteristics.

The study continues in the same manner by considering CTRW as a source of the velocity distribution. BTCs from the previous simulation are fitted with the CTRW model with TPL transition time distribution. It is obvious, that the transition time on a grid can be translated to velocities. Consequently, the derived velocity distribution (Fig. 5.3) is applied to GCT and the BTCs are compared. Finally, it is concluded that GCT accounts for physical phenomena in a natural way.

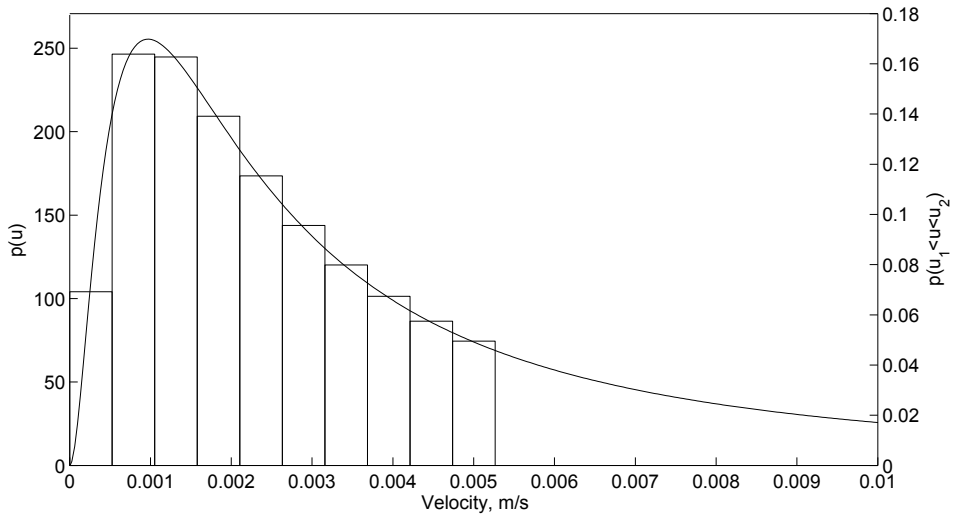

Figure 5.3: TPL velocity distribution (solid line, left axis) and its discretized form applied for GCT (bins,right axis).

5.5 Conclusions and future directions

This study focuses mainly on the Generalized Continuum Transport model and its parameter space. It was important to provide a thorough description of GCT focusing on its attractivity in terms of mathematical investigations, flexibility with respect to construction of the parameter space, accuracy of anomalous transport quantification and relation to the medium's characteristics. It has been demonstrated how the modeling choice can be eliminated by introduction of the parameter space in terms of the GCT framework.

The benefits of GCT can be summarized in a few points:

1. Continuous in both space and time which is useful for mathematical investigations.

2. Has existing models as a limit or a subset.

3. Suitable for accurate flow quantification especially the tailing effect of anomalous transport.

4. Flexible in terms of accuracy and complexity: a researcher can always select between accuracy and complexity.

5. The form of the parameter space can be constrained and related to the medium's properties.

6. The form of the parameter space can always be changed in order to match the medium's construction and flow complexity.

Though the parameter space of GCT is, in general, continuous, in Papers C and D it is investigated in its discretized form in order to assess the model numerically. Thus, GCT is studied in a form of the multiple continuum limit. It is, therefore, beneficial to consider the parameter space in its continuous form through, for example, the Lagrangian form, as it is done in Paper A. We believe that this is an interesting direction for future investigations.

At the same time, it is useful to consider more forms of the parameter space and relations to the medium's nature. This can include 2D and 3D simulations of plume propagation through more complex porous structures combined from both small pores and larger structures, as done in 1D in paper C for the multi-zone medium.

In Papers C and D only a part of the GCT's parameter space is related to the network's characteristics: the void space distribution and the velocity distribution are extracted directly from the construction of the network, while the mass exchange term is a result of the BTCs fitting. It is, therefore, important to address this issue as well, such that the whole parameter space is related to the medium's macro and microscale properties.

Finally, we hope that Generalized Continuum Transport is an interesting framework from both mathematical (continuity) and engineering (accuracy) point of view.

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Part II

Included papers

Paper A

On the relationship between multiple porosity models and Continuous Time Random Walk

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In *Proceedings of the XVIII International Conference on Water Resources, CMWR2010* (2007)

XVIII International Conference on Water Resources
CMWR 2010
J. Carrera (Ed)
CIMNE, Barcelona 2010

ON THE RELATIONSHIP BETWEEN MULTIPLE POROSITY MODELS AND CONTINUOUS TIME RANDOM WALK

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Key words: Anomalous transport, CTRW, dual porosity

Summary. We derive a multiple porosity model based on the continuous time random walk model (CTRW). In particular, we show how the parameters of the multiple porosity models relate to the transition probability function which is at the heart of the CTRW formulation. A simple example is included to illustrate the results.

1 INTRODUCTION

Models for particle transport associated with fluid flow in porous media are essential for a wide range of applications spanning exploitation of groundwater resources to paper production and fuel cells. While many of the challenges in these applications relate to the simultaneous flow of multiple fluids through the pore space, even transport of a passive component flowing with a single fluid is not properly understood on scales above that at which the porous structure can be resolved (see e.g. the special issue [1]).

Numerous experiments indicate that the solutions to the Advection-Dispersion Equation (ADE) and its modifications do not capture the full complexity of transport (see e.g. [2] and references therein). The last decade, the Continuous Time Random Walk (CTRW) model has been advocated as a general framework to address transport in porous media [2]. This is supported by the equivalence to the generalized master equation (GME) [3], showing that the solutions of CTRW must include the solution of all other deterministic transport models either through equivalence or as a subset.

However, in practical applications, multiple porosity models remain much more widespread, due to their simple implementation in existing code packages, as well as their simple intuitive interpretation [4, 5].

In this paper, we show an explicit relationship between multiple porosity models and CTRW. This relationship goes beyond the usual analysis, which shows how CTRW converges to certain fractional differential equations in appropriate limits, by defining a multiple porosity model which is identified as identical to CTRW under a certain discretization in its Lagrangian formulation. This is achieved through considering generalized multiple porosity models with potentially infinitely many continua.

Thus, we formulate a duality where CTRW is seen as a spatial discretization of transport, while retaining the exact structure of the subscale velocity distribution. In contrast, multiple

porosity models with a finite number of continua can be considered as spatially continuous models with a discrete approximation to the velocity distribution.

We structure the presentation as follows. In the next section, we give the generalization of multiple porosity models we exploit in this paper. In section 3, we give a brief reminder of the main formulations of CTRW. Finally, in Section 4, we show the explicit relationship between CTRW and multiple porosity models.

2 MULTIPLE POROSITY MODELS

Multiple continua models are the intuitive generalization of single continua models. The idea was first presented by Barenblatt [6], and has since been widely used, not only for particle transport but also for multi-phase flow and thermal transport.

Most commonly, multiple porosity models are applied to only two continua, and these are then identified as e.g. the fracture continua and the matrix continua. The equation for mass transport in the fracture continua (identified by subscript 1) can then be written as

$$\partial_t m_1 + \nabla \cdot (\boldsymbol{u}_1\, c_1 - \boldsymbol{D}_1 \nabla c_1) = \kappa\, (c_2 - c_1), \tag{1}$$

with the equivalent transport equation for the matrix continua (identified by subscript 2)

$$\partial_t m_2 + \nabla \cdot (\boldsymbol{u}_2\, c_2 - \boldsymbol{D}_2 \nabla c_2) = \kappa\, (c_1 - c_2). \tag{2}$$

In equations (1-2), we may relate masses and concentrations by the porosity ϕ and the fraction of the porosity which is associated with each continua φ_i, thus using ρ to denote density, $m_i = \rho \phi \varphi_i c_i$. The fluxes $\boldsymbol{u}_i$ are usually determined from Darcy's law, while the dispersion tensors $\boldsymbol{D}_i$ and interaction coefficient κ are (possibly flux dependent) properties of the medium. We take these parameters as known herein.

The natural generalization of the dual porosity models is the n-porosity model employed by Gwo for contaminant transport [5] and by Pruess for thermal transport [4]. This model can be concisely written as

$$\partial_t m_i + \nabla \cdot (\boldsymbol{u}_i\, c_i - \boldsymbol{D}_i \nabla c_i) = \textstyle\sum_{j=1}^{n} \kappa_{i,j}\, c_j, \qquad \text{for all} \quad i = 1..n\,. \tag{3}$$

The parameters $\kappa_{i,j}$ must be positive (when $i \neq j$) for dispersive processes, with $\sum_j \kappa_{i,j} = 0$. Further, we mass conservation implies $\sum_i \kappa_{i,j} = 0$. By definition, we also have the constraint that $\sum_i \varphi_i = 1$.

Herein, we will further generalize Equation (3) by considering not only a finite number of continua, but indeed infinite families of continua. On one hand, this is simply a formal generalization, but it may also be given physical interpretations as we will see below. When we treat the index as a continuous variable, we will denote it by ω, which is assumed to be in the space Ω. Our independent variables are then functions of both physical and parameter spaces, in addition to time, e.g. $m = m(\boldsymbol{x}, \omega, t)$, where $(\boldsymbol{x}, \omega, t) \in \mathbb{R}^d \times \Omega \times \mathbb{R}^+$. The continuous generalization of Equation (3) is then stated as

$$\partial_t m + \nabla_{\mathrm{x}} \cdot (\boldsymbol{u}\, c - \boldsymbol{D} \nabla_{\mathrm{x}} c) = \textstyle\int_\Omega \kappa(\omega, \omega') c(\omega')\, d\omega'. \tag{4}$$

The subscript on the differential operators emphasizes that the differential is with respect to the spatial coordinate, as opposed to the parameter space coordinate ω.

The generalized multiple porosity model can also be written such that it accommodate non-

passive particles by replacing the integral transform on the right hand side by a non-linear operator, which we write as:

$$\partial_t m + \nabla_{\mathrm{x}} \cdot (\boldsymbol{u}\, c - \boldsymbol{D}\nabla_{\mathrm{x}} c) = N\big(m|_{x,t}\big). \tag{5}$$

3 CONTINUOUS TIME RANDOM WALK

The Continuous Time Random Walk (CTRW) models represent a distinct departure from the modeling philosophy of Section 2. Instead of looking at the deterministic movement of a concentration of particles in a continuum, CTRW considers the transition probabilities for particles between discrete points.

The usual CTRW derivation lets the probability density R of a particle arriving at some point in time be related to the history of the problem [7]:

$$R(\boldsymbol{x}, t) = \sum_i \int_0^t \psi_{CTRW}(\boldsymbol{x}_i', t') R(\boldsymbol{x} - \boldsymbol{x}_i', t - t')\, dt' \,. \tag{6}$$

Here we use a summation over space to emphasize that the spatial points are discrete and countable, and the transition probability is given by ψ_{CTRW}. From this equation, the probability density P of a particle being at a point is deduced from the probability that it has not transitioned to a different point,

$$P(\boldsymbol{x}, t) = \int_0^t \Psi(t') R(\boldsymbol{x}, t - t')\, dt', \tag{7}$$

where the probability of not transitioning is defined as

$$\Psi(t) = 1 - \int_0^t \sum_i \psi_{CTRW}(\boldsymbol{x}_i', t')\; dt', \tag{8}$$

Continuous time models thus shift the emphasis away from the traditional view of advection and dispersion on a continuum scale, towards a concept of a spectrum of transition times. These are useful concepts and ideas, and they motivate our desire to incorporate this approach within multiple porosity models.

4 MULTIPLE POROSITY AND CTRW

We have seen in sections 2 and 3 that while both multiple porosity (MP) models and continuous time random walk aim at describing transport phenomena, they are parameterized by different functions. Indeed, the main parameters of concern to us in the MP model are the flux distributions $\boldsymbol{u}$; the distribution of continua (porosity) φ_i; and the kernel of the continua exchange term κ. In contrast, the important parameter of the CTRW model is the transition probability function ψ. Recalling that our aim is to be able to reproduce the results of CTRW within a MP model, we will in this section show how to chose the parameters of the multiple porosity model given a transition probability function ψ_{CTRW}.

Our approach will be to manipulate the MP model, by change of variables, rewriting the equation in a Lagrangian framework, and finally introducing a low-order quadrature. This will lead to equations equivalent to Equations (6), and we can thus identify the relationship

between the parameters of the two models. Since Equation (6) is discrete in space, we will use a form of the MP porosity model where the parameter space has both continuous and discrete components.

As a preliminary note, we point out that the non-linear MP model is related to the Boltzmann equation, by identifying $\Omega = \mathbb{R}^d$, and interpreting it as the (discrete) flux space, e.g. $\omega = \boldsymbol{u}_i$. We then obtain from a dispersion free Equation (5)

$$\partial_t m_i + \nabla_{\mathrm{x}} \cdot (\boldsymbol{u}_i\, c) = N_i\big(m|_{\boldsymbol{x},t}\big). \tag{9}$$

Up to the scaling between flux and velocity, Equation (9) is a discrete Boltzmann equation with no body forces. A common approximation to the collision term of the Boltzmann equation is the Bhatnagar-Gross-Krook (BGK) collision operator [8], which takes the form

$$N_{i,BGK}\big(m|_{\boldsymbol{x},t}\big) = \tfrac{\langle m\rangle\, f_{i,eq} - m_i}{\tau}. \tag{10}$$

Here angled brackets implies integration and summation over the parameter space Ω;

$$\langle m\rangle = \langle m\rangle(\boldsymbol{x},t) = \int_\Omega m(\boldsymbol{x},\omega,t)\, d\omega = \sum_i \int_{\Omega_c} m_i(\boldsymbol{x},\omega_c,t)\, d\omega$$

Here, Ω_c refers to the continuous part of Ω. Further, the equilibrium distribution refers to the distribution in Ω, such that $f_{eq} = f(\omega;\boldsymbol{x},t)$. Note that for dispersive processes, Equation (10) implies that $f_{eq} = \varphi$, since $m = \rho\phi\varphi c$. The characteristic time-scale of relaxation is given by τ, and we will include this time-scale in the parameter space, thus $\Omega = \mathbb{P}\times\mathbb{R}^+$, and $\omega = (i,\tau)$. Since τ is now dependent on the parameter space, we must be careful with how we formulate the collision operator in order to retain mass balance. Then it is necessary to consider not the integral mass $\langle m\rangle$, but rather the weighted average $\langle\tau^{-1}m\rangle$. From a Boltzmann perspective, this corresponds to the mass (per time) entering collisions. From our perspective, this represents the mass (per time) leaving a continuum. Similarly, we are therefore also interested in not only the equilibrium distribution, but also how mass is distributed from collisions,

$$f_{i,coll}(\tau) = \tfrac{\tau^{-1} f_{i,eq}(\tau)}{\langle\tau^{-1} f_{eq}\rangle}. \tag{11}$$

We will in the continuation suppress the dependence on i or τ when it is clear from the context. Motivated by this analogy to the Boltzmann equation, we will investigate a collision term of the type

$$N_{CTRW}\big(m|_{\boldsymbol{x},t}\big) = \langle\tau^{-1}m\rangle\, f^*_{coll} - \frac{m}{\tau}. \tag{12}$$

We recognize the first term on the right hand side as the source to the continua from exchanges, while the second term represents the loss term.

Using the collision term suggested in Equation (12) in the MP model given in Equation (5), and by transforming the equation from using a fluid flux to particle velocity as parameter, so that $\boldsymbol{v}_i = (\phi\varphi_i)^{-1}\boldsymbol{u}_i$, we can write the dispersion free MP model in terms of the mass $m = m_i(\boldsymbol{x},\tau,t)$,

$$\partial_t m + \nabla_x \cdot (\boldsymbol{v}\, m) = \langle\tau^{-1}m\rangle\, f_{coll} - \frac{m}{\tau}. \tag{13}$$

It is convenient to change dependent variables so that Equation (13) is written in terms of the mass lost to exchange, $p_i(\boldsymbol{x},\tau,t) = \tau^{-1}m_i(\boldsymbol{x},\tau,t)$ in stead of the mass distribution, which

gives the equation

$$\partial_t p + \nabla_x \cdot (\boldsymbol{v}\, p) = \frac{\langle p \rangle f_{coll} - p}{\tau}. \tag{14}$$

This equation governs the evolution of the mass per time changing continua p, and has the same structure as the Boltzmann equation with the BGK relaxation term. This quantity is related to the *arrival* probability R solved for in the CTRW model, as we can see from Equation (12). However, Equation (14) is of a very different form than Equation (6).

We now proceed by writing Equation (14) on a Lagrangian form. By integrating Equation (14) along characteristics from time $t - \epsilon\tau$ to t, we obtain

$$p_i(\boldsymbol{x}, \tau, t) = p_i(\boldsymbol{x} - \boldsymbol{v}_i \epsilon\tau, \tau, t - \epsilon\tau) + \int_{-\epsilon\tau}^{0} N_{i,CTRW}\left(\tau\, p_i|_{x+v_i\tau', t+\tau'}\right) d\tau'. \tag{15}$$

While in general, ϵ is some small parameter, it is helpful to keep in mind the special case where $\epsilon = 1$, as this leads to needed simplifications the later expressions. This is equivalent to considering a Lagrangian step which is exactly equal to the inverse exchange rate.

To treat the integral in Equation (15), we approximate the integral by simple quadrature. Let the integral over the collision operator be approximated by its lower limit;

$$\int_{-\epsilon\tau}^{0} N_{i,CTRW}\left(\tau\, p_i|_{x+v_i\tau', t+\tau'}\right) d\tau' \approx \epsilon\tau\, N_{i,CTRW}\left(\tau\, p_i|_{x-v_i\epsilon\tau, t-\epsilon\tau}\right). \tag{16}$$

Then substituting the definition of the exchange term we obtain from Equation (15)

$$\begin{aligned} p_i(\boldsymbol{x}, \tau, t) = {} & (1 - \epsilon) p_i(\boldsymbol{x} - \boldsymbol{v}\epsilon\tau, \tau, t - \epsilon\tau) \\ & + \epsilon \langle p \rangle (\boldsymbol{x} - \boldsymbol{v}_i \epsilon\tau, t - \epsilon\tau)\; f_{i,coll}(\tau; \boldsymbol{x} - \boldsymbol{v}_i \epsilon\tau, t - \epsilon\tau). \end{aligned} \tag{17}$$

We see that for homogeneous problems, where the exchange term is independent of space, the last term of Equation (17) is decoupled. When we chose the discretization parameter $\epsilon = 1$, the first term on the right hand side of Equation (17) is zero, which allows us to obtain an equation for the evolution of the total mass by integrating over Ω, leading to:

$$\langle p \rangle(\boldsymbol{x}, t) = \sum_i \int_0^t \langle p \rangle (\boldsymbol{x} - \boldsymbol{v}_i \tau, t - \tau)\, f_{i,coll}(\tau; \boldsymbol{x} - \boldsymbol{v}_i \tau, t - \tau)\, d\tau. \tag{18}$$

By changing the variables of integration we can go from a velocity formulation to a spatial formulation, with $\boldsymbol{x}_i' = \boldsymbol{v}_i \tau$ and $t' = \tau$.

$$\langle p \rangle(\boldsymbol{x}, t) = \sum_i \int_0^t \langle p \rangle (\boldsymbol{x} - \boldsymbol{x}_i', t - t')\, f_{i,coll}(t')\, dt'. \tag{19}$$

Here, we have assumed that the collision operator is homogeneous in space-time.

For Equation (19) to be equivalent to Equation (6), we identify the distribution ψ_{MP} as the CTRW distribution,

$$f_{i,coll}(t) = \psi_{CTRW}(\boldsymbol{x}_i, t). \tag{20}$$

We note by comparing equations (6) and (19) that the probability R of a particle arriving at a point in the CTRW model satisfies the same equation as the mass change $\langle p \rangle$ at a point in a discrete-continuous form of the MP model as given in Equation (19). For spatially discrete distributions as given in Equation (20), integration needed to convert from arrival probability R to a conservative probability P is analogous to the relationship between mass collision densities p to physical masses m. Thus we have reached the conclusion that the CTRW can be interpreted as a spatial discretization of an approximate MP model in Lagrangian coordinates, where the interaction term is evaluated by one-sided quadrature.

We summarize the relationship between the parameters of the MP and the CTRW models in Table 1, together with several of the intermediate distributions used in the derivation. The

key results are given in bold.

Property	Expression
Multiple Porosity Equation	$\partial_t m_i + \nabla_{\mathrm{x}} \cdot (\rho\, \boldsymbol{u}_i\, c) = \sum_j \int_{\Omega_{\mathbf{c}}} \kappa_{i,j}(\omega_c, \omega') c(\omega')\, d\omega'$
Parameter space	$\Omega = \mathbb{P} \times \mathbb{R}^+$
Parameter variable	$\omega = (i, \tau)$
Lagrangian transport kernel	$f_{i,coll}(t) = \psi_{CTRW}(\boldsymbol{x}_i', t)$
Equilibrium distribution	$f_{i,eq}(\tau) \sim \tau\, \psi_{CTRW}(\boldsymbol{x}_i', \tau)$
Discrete structure	$\varphi_i(\tau) \neq 0 \Rightarrow \boldsymbol{u}_i \tau = \boldsymbol{x}_i' \rho \phi \varphi_i(\tau)$
Flux density relation	$\varphi_i(\tau) = f_{i,eq}(\tau) = \tau\, \psi_{CTRW}\left(\frac{\boldsymbol{u}_i \tau}{\phi \varphi_i(\tau)}, \tau\right)$
Exchange term kernel	$\kappa_{i,j}(\tau, \tau') = \frac{1}{\tau'} \psi_{CTRW}\left(\frac{\boldsymbol{u}_i \tau}{\phi \varphi_i(\tau)}, \tau\right) - \frac{\delta(\tau - \tau')}{\tau} \delta_{i,j}$

Table 1: The main parameter functions of the MP model expressed in terms of the parameter functions of the CTRW model are give in the table in bold. Various other expressions of interest from this section are also provided.

5 EXAMPLE CALCULATION

To illustrate the relation between the parameters of CTRW and MP models we investigate a simple representation of a 2D network with a regular triangular structure. With flow aligned with the network, this network has two types of pore throats: parallel and inclined to the flow direction.

In such a synthetic case the fluid after complete mixing in a pore node will with probability $\eta_1 = 2/3$ go through the inclined pore, and with probability $\eta_1 = 1/3$ go through a parallel pore. The corresponding travel distances are denoted Δx_1 and Δx_2, with $\Delta x_2 = 2\Delta x_1$. Similarly, we denote the travel times Δt_1 and Δt_2.

Considering the described porous system in the CTRW framework we first observe that for this simple network, we only have two continua, and that the distribution of transit times is also discrete. Thus we replace the continuous time derivation from Section 4 with an equivalent discrete time random walk formulation. The transition probability is then given as

$$\psi(x_i', t') = \begin{cases} \eta_1 & \text{if} \quad x_i' = \Delta x_1 \quad \text{and} \quad t_i' = \Delta t_1 \\ \eta_2 & \text{if} \quad x_i' = \Delta x_2 \quad \text{and} \quad t_i' = \Delta t_2 \end{cases}$$

Following the calculations in Table 1 we can rewrite the exchange term kernel on the form

$$\kappa_{i,j} = \frac{\eta_i}{\Delta t_j} - \frac{\delta_{ij}}{\Delta t_i}$$

Figure 1 shows a comparison between the break-through curves obtained by a network model as described, together with the equivalent dual-porosity model. The parameters have been chosen to be characteristic of homogeneous sand. While this is a relatively simple problem, the example nevertheless validates the connection between CTRW and MP models derived in Section 4. We also note that for these parameters, even though the coupling term κ is relatively strong, the curves nevertheless show a devitation from the error function predicted by a single porosity model.

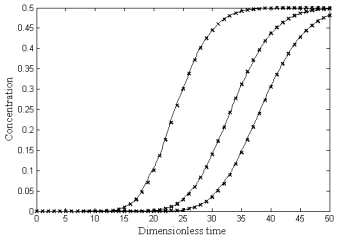

Figure 1. Concentration profiles obtained different distances from the injection point. Results from network model (lines) and dual-porosity model (crosses).

5 DISCUSSION

We summarize the main results and observations herein:

1. Given a suitable approximate Lagrangian form, the parameters of the multiple porosity model can be obtained from the parameters of the continuous time random walk model.
2. Conversely, the continuous time random walk model can be seen as a spatial discretization of an approximate Lagrangian form of the multiple porosity model.
3. A suitable interpretation of the different continua in the multiple porosity model is that they represent fluxes and expected particle travel times between change in flux field.
4. The kernel κ of the exchange transform can be expressed explicitly given the flux density φ.
5. In practice, only a (small) finite number of continua are used in multiple porosity models. The multiple porosity model can then be seen as a flux space discretization of the underlying transition time distribution ψ, as opposed to continuous time random walk which is a spatial discretization.

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Graphic design: Communication Division, UiB / Print: Skipnes Kommunikasjon AS

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ISBN: 978-82-308-3820-4