Solute transport within porous biofilms: diffusion or dispersion?

by

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Abstract

Many microorganisms live within surface-associated consortia, termed biofilms, that can form intricate porous structures interspersed with a network of fluid channels. In such systems, transport phenomena, including flow and advection, regulate various aspects of cell behaviour by controlling nutrient supply, evacuation of waste products and permeation of antimicrobial agents. This study presents multiscale analysis of solute transport in these porous biofilms. We start our analysis with a channel-scale description of mass transport and use the method of volume averaging to derive a set of homogenized equations at the biofilm-scale. We show that solute transport may be described via two coupled partial differential equations for the averaged concentrations, or telegrapher’s equations. These models are particularly relevant for chemical species, such as some antimicrobial agents, that penetrate cell clusters very slowly. In most cases, especially for nutrients, solute penetration is faster, and transport can be described via an advection-dispersion equation. In this simpler case, the effective diffusion is characterised by a second-order tensor whose components depend on: (1) the topology of the channels’ network; (2) the solute’s diffusion coefficients in the fluid and the cell clusters; (3) hydrodynamic dispersion effects; and (4) an additional dispersion term intrinsic to the two-phase configuration. Although solute transport in biofilms is commonly thought to be diffusion-dominated, this analysis shows that dispersion effects may significantly contribute to transport.
I. INTRODUCTION

Biofilms are sessile communities of microbes that develop on solid or liquid interfaces, embedded within extracellular polymeric substances (EPS) [6]. These aggregations of microorganisms represent the dominant form of microbial life on Earth and have a considerable sanitary, ecological and economic impact. Effects can be desirable (wastewater processes, bioremediation, industrial and drinking water treatment, sequestration of carbon dioxide) or undesirable (paper manufacture, microbially influenced corrosion within pipelines, heat exchangers, or on ships) and, potentially, harmful (contamination in the food industry, disease, chronic infections, sustainability of water supply networks). Within the last few decades, understanding and controlling biofilm growth has emerged as a major scientific challenge. An important component of this challenge is to understand how chemical species and particles are transported within biofilms, in order to: (1) elucidate their resistance to antimicrobial agents; (2) design efficient control and staining strategies; (3) develop reliable growth models; and (4) describe the exchange of signalling molecules or genetic material between cells. These transport phenomena generally result from coupled biological, physical and chemical processes occurring over a large spectrum of temporal and spatial scales.

Porous biofilms demonstrate well the degree of heterogeneity intrinsic to these structures, and the complexity of the corresponding transport processes. In the early days of biofilm research, mathematical and conceptual models pictured these consortia of microorganisms as a homogeneous coating of a solid surface. Later on, experiments showed that biofilms can form intricate architectures. For example, Stoodley, deBeer and Lewandowski [43] used confocal laser scanning microscopy (CLSM) to perform a particle image velocimetry analysis and map the velocity field within biofilms grown under different conditions. They reported fluid flow inside biofilm channels and observed situations in which water flowed against the main current of the bulk water phase. Advances in optical coherence tomography (OCT) suggest even more complicated geometries. Wagner et al. [48] analyzed the structure of heterotrophic biofilms on relatively large volumes using OCT and revealed an incredible level of complexity. It has also emerged, for example see discussions by Plalková [32], that wild strains in real environments tend to form more heterogeneous structures than laboratory strains. These results have led to the idea that biofilms are complex permeable structures, rather than dense impermeable gel-like layers. Therefore, a few recent models treat biofilms
as porous materials in which fluid flow is considered. For example, Dupin, Kitanidis and McCarty [13] and Thullner and Baveye [44] determined the velocity field within the bulk fluid phase, viscosity $\mu_f$, and the biofilm, viscosity $\mu_b$, by considering a fictitious weighted viscosity within the biofilm phase, $\mu_b = \gamma\mu_f$ with $\gamma \geq 1$. Kapellos, Alexiou and Payatakes [24] developed a simulator that couples a cellular automaton with multiscale methods. They used a single-domain volume-averaged formulation, originally developed for Darcy-scale fluid-porous interfaces (see in [16]), to model the fluid flow within the bulk fluid and biofilm phases. Surprisingly, these studies have focused on momentum transport, and have not addressed the consequences of biofilm permeability on mass transport. Transfer of a molecule, or a Brownian particle, within these structures is influenced by a number of mechanisms, including advection. In this study, our goal is to understand the physics of these transport phenomena at the biofilm-scale. We focus primarily on passive solute transport, but also discuss the effect of microorganisms actively restricting the penetration of biocides within the cell clusters.

Passive solute transport in biofilms, regardless of their architecture, is often characterised by the ratio, $D_e/D_{aq}$, of the effective, $D_e$, and reference (culture medium or growth fluid), $D_{aq}$, diffusion coefficients. Various experimental techniques have been adapted to the calculation of the effective diffusion coefficient. Bungay, Whalen and Sanders [3] used the oxygen microelectrode technique. Matson and Characklis [28] used a two-chamber method to measure oxygen and glucose diffusion coefficients in sludge flocs. de Beer et al. [11] used a combination of oxygen microelectrode measurements and CLSM to correlate the concentration gradients with the structure of aerobic biofilms. Lawrence, G. M.Wolfaardt and Korber [26] observed the diffusion of fluorescein and fluor-conjugated dextran in *Pseudomonas* using fluorescence recovery after photobleaching (FRAP) and CLSM. Bishop, Zhang and Fu [2] calculated the effective diffusion coefficient from the structure of frozen 10 – 20 $\mu$m slices of biofilm. Stewart, Davison and Steenbergen [42] measured the diffusion coefficient of tagged daptomycin in cells clusters of *Staphylococcus epidermis* using CLSM. Recently, methods involving nuclear magnetic resonance (NMR) were proposed to obtain effective diffusion coefficients in situ [29, 37]. Advances in X-ray microtomography also offer new perspectives for studying in situ transport properties in porous structures Davit et al. [9], Iltis et al. [22] and for estimating the corresponding diffusion coefficients.

Although $D_{aq}$ is well defined for a given temperature, solute, and growth medium, the
Table I. Examples of studies in which dispersion effects have been observed in biofilms and biopellets.

<table>
<thead>
<tr>
<th>Object</th>
<th>Species</th>
<th>Technique</th>
<th>Diffusion</th>
<th>Papers</th>
</tr>
</thead>
<tbody>
<tr>
<td>Biofilm</td>
<td>NaNO₃</td>
<td>2-chamber</td>
<td>0.1 &lt; De/Daq &lt; 1.1</td>
<td>Horn and Morgenroth [20]</td>
</tr>
<tr>
<td></td>
<td>NaCl</td>
<td>µelectrodes</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>Oxygen</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Biopellets</td>
<td>Oxygen</td>
<td>µelectrodes</td>
<td>0.2 &lt; De/Daq &lt; 1.5</td>
<td>Hille et al. [18]</td>
</tr>
<tr>
<td>Biofilm/agar</td>
<td>Gd-DTPA</td>
<td>MRI</td>
<td>De/Dagar = 1.44</td>
<td>Ramanan et al. [36]</td>
</tr>
<tr>
<td>Biofilms</td>
<td>Review</td>
<td>Review</td>
<td>0.11 &lt; De/Daq &lt; 2</td>
<td>Melo [30]</td>
</tr>
</tbody>
</table>

The interpretation of De is ambiguous. Active biological processes, such as uptake rates, or physico-chemical properties of the biofilm, the solute and the bulk fluid phase are difficult to correlate with De. Many studies have focused on identifying those parameters that most influence De. Several authors have proposed empirical relationships between De/Daq and the biofilm density ρ for passive transport [15]. Hinson and Kocher [19] used the fraction of EPS as an additional parameter. Stewart [40] investigated the influence of chemical properties, such as charge of the EPS or molecular weight of the solute molecules. These correlations could be extended in many ways to account for other biochemical processes. Such formulae are extremely important because they can be widely used by experimentalists. However, many fundamental aspects of passive transport are still a matter of debate [30]. For example, the following points have received little attention from a mathematical modelling point of view:

- Biofilms are known to form layered or stratified structures [53], with larger densities near the solid surfaces. This stratification means that the diffusion coefficient within the cell clusters varies in space and raises several fundamental questions: how does stratification influence De? Is it valid to use a single effective value of the diffusion coefficient, or should a spatially-resolved coefficient be used?

- Is it possible to characterise solute transport in terms of the ratio De/Daq when there is fluid flowing within the biofilm? Is it even possible to define an effective diffusion in this case?

In addition to the above theoretical issues, there is often ambiguity in the interpretation
of experimental estimates for $D_e$. Recently, Wagner et al. [48] emphasised this problem by comparing estimates of biofilm porosities obtained using OCT and CLSM. For a Reynolds number of 4000 in the bulk fluid phase, the porosity of the biofilm was found to be about 0.98 using CLSM and 0.35 using OCT. The authors suggest that OCT provides a more reliable framework for studying biofilm structures because it does not require fluorescence staining, and therefore does not rely on the transport properties of the biofilm, and is not limited by laser penetration depth. This is an important observation because CLSM is widely used to measure structural biofilm properties, and this may lead to erroneous conclusions. These results have wider implications that go beyond the issue of CLSM applicability: they suggest that caution should be exercised when interpreting experimental data for biofilms. All the techniques discussed above differ in terms of their physical significance and parameters, such as $D_e$, need to be defined in relation to a specific experiment. Particularly relevant to this discussion is the spatial resolution of the experimental method under consideration. For example, the NMR technique used in [37] has an in-plane resolution of 7.5 by 250 µm. A measurement performed using X-ray microtomography or OCT could resolve to several micrometers. CLSM can achieve a similar resolution, but this will be strongly dependent on the fluorescent staining. Two-chamber experiments only capture bulk information within each chamber. The parameters that are measured using these techniques are averaged over different volumes, and their physical interpretation is different. For instance, if the biofilm contains fluid channels of approximate width 10 µm, then a technique with a resolution of 100 µm is measuring a concentration field and/or a diffusion coefficient averaged over both the cell clusters and the channels. On the other hand, a technique with a resolution of several micrometers can delineate between the two and/or provide a local diffusion coefficient for layered cell clusters. Experimental studies should carefully address these issues.

In order to expand on the idea that $D_e$, as reported in the literature, is not a well-defined quantity, we now focus on studies that have previously reported peculiarities in the ratio $D_e/D_{aq}$. In most cases, the ratio $D_e/D_{aq}$ ranges between 0.1 and 1 (e.g., in [41]). In these situations, the path of a solute molecule in a cell cluster is constrained by the presence of obstacles (cells, extracellular polymeric substances, abiotic particles) and a notion of tortuosity can be invoked [30]. Interestingly, in some low-density biofilms and in fungal biopellets, this ratio has also been reported to be larger than unity, cf. Table I. For example, Ramanan et al. [36] estimated the diffusion coefficient of a complex of Gadolinium
and DiethyleneTriamine Pentaacetic Acid (Gd-DTPA) using magnetic resonance imaging with an in-plane resolution of 150 µm by 150 µm. They observed the concentration fields in agar, a highly permeable gel, and in a phototrophic biofilm. The diffusion coefficient in the biofilm was found to be larger than that in the highly permeable gel. Using this comparison, the authors deduced that transport in the biofilm was by both diffusion and advection. Melo [30] argues that the tortuosity, Λ, defined by $D_e = D_{aq}/\Lambda$, can be lower than unity if the solute undergoes convection inside the biofilm. This is an interesting idea, but it also suggests that a lot of physics is hidden within $D_e$ and that a notion of tortuosity alone might not be sufficient. Hydrodynamic dispersion could be used to interpret these results if the Péclet number, $P_e = \nu d/D_{aq}$, where $\nu$ is an average velocity and $d$ a characteristic length, is sufficiently large. For example, in Fig 5 in [43], the Péclet number, for oxygen transport at 25°C, is approximately 100; therefore suggesting that hydrodynamic dispersion will be important. In the case of the biopellets, the flow is not limited by the EPS, and even larger ratios, $D_e/D_{aq} > 1$, have been reported when the cell density is relatively low (e.g., in [18] Fig 3 p. 1207).

Even when $D_e/D_{aq} < 1$, it is not straightforward to determine the relative contributions of diffusion and advection to the transport. It is commonly accepted that $D_e/D_{aq} < 1$ corresponds to a diffusion-dominated transport. For instance, Horn and Morgenroth [20] clearly state that “[...] a convective transport would have resulted in $D_e/D_{aq} > 1$. The results presented indicate that for biofilms older than a few days and with mean biofilm density higher than 20 kg/m$^3$ convective transport can be neglected”. We question this interpretation. In the case of porous biofilms, $D_e/D_{aq} < 1$ means that the combined effects of the advective and diffusive “components” (a clear definition of these “components” is given later in this paper) leads to a reduction in the diffusion coefficient, but this does not mean that the advective component is negligible compared to the diffusive one. A ratio smaller than unity, say $D_e/D_{aq} = 0.9$, may very well mean that $D_{e, diffusion}/D_{aq} = 0.2$ without advection effects. For example, if hydrodynamic dispersion occurs within the channels, then the transition from $D_e/D_{aq} < 1$ to $D_e/D_{aq} \geq 1$ is continuous, and there is a region in parameter space for which $D_e/D_{aq} < 1$ is compatible with advection. This suggests that we need additional experimental data, and a clear definition of $D_e$ that can be used to interpret such results.

In this paper, we propose such a definition for $D_e$. Our interpretation requires that biofilms
should not be defined as cell clusters alone, but as a two-phase mixture of a cell cluster phase \(\omega\) interspersed with a fluid-flow-channel phase \(\kappa\). We develop a multiscale strategy to derive an effective diffusion tensor for this situation. Within the cell-EPS matrix (i.e., the cell clusters) the solute is transported by diffusion alone, but the diffusion coefficient can vary “arbitrarily” (although smoothly) in space. In the channels, the solute is transported by advection and diffusion. We apply volume averaging to obtain a set of homogenized models, i.e., we use a technique that has previously been successfully used to upscale transport phenomena within porous media, biofilms and biological tissues [1, 54, 56]. We show that transport can be described in terms of a two-equation model or telegrapher’s equations when the solute slowly penetrates the cell clusters or in porous media, e.g., when the microorganisms or the EPS are restricting its penetration. We also show that these models have a time-asymptotic behaviour that can be described by a single advection-diffusion equation and provide a biophysical interpretation of the analytic form of the effective diffusion tensor.

The remainder of this study is organized as follows. Firstly, we detail our microscale problem. A representative elementary volume (REV) of the system is presented in Fig 1 and the corresponding mathematical model at the channel-scale is presented in section II. We are interested in hierarchical systems, for which \(L_\kappa \ll R \ll L\); where \(L_\kappa\) is a characteristic width of the channels, \(R\) is the radius of the REV and \(L\) is a characteristic macroscale length for the biofilm. In section III, we perform a perturbation analysis, termed the volume averaging with closure technique, to derive the different macroscale models. For brevity, the key results are presented in the main body of the text, while technical details are provided in the Appendix or in specific references. The paper concludes with a discussion of the potential applications of these models and their limitations.

II. MICROSCALE FORMULATION

As discussed previously, the biofilm is decomposed into two distinct phases: a cell-EPS matrix phase \(\omega\) and the fluid channels phase \(\kappa\) (see Fig 1). Within the cell-EPS matrix phase, the solute is transported by diffusion alone but the diffusion coefficient can vary in space. In the channel phase, the solute is transported by diffusion and advection. Delineating explicitly between the bulk water-phase and the channels is obviously an important problem that should be carefully addressed in the future. However, for the purposes of this study,
Figure 1. Schematic diagram highlighting the multiscale nature of biofilms. Two different ways of averaging are presented: on the left, the averaging volume is defined over the entire height of the biofilm, with a diffusion coefficient within the cell clusters which varies with depth; on the right, the averaging volume is defined on a small portion of the biofilm, this is appropriate if the diffusion coefficient within the cell clusters varies slowly throughout the biofilm and if some separation of scale constraints are satisfied. Three spatial scales can be identified: the biofilm-scale, the channel-scale and the cell-scale. Each region illustrates a representative elementary volume of the corresponding larger scale. In this work, we focus on the upscaling from the channel-scale to the biofilm-scale.

we consider an idealised channel phase and suppose that all interfaces are static. This assumption is valid if the timescales associated with the transport phenomena and the growth processes are markedly different (e.g., in [51]), and can be further justified by the stated aim to understand mass transport itself, rather than its coupling with growth.

By considering conservation of mass for a given species, the following system of equations
can be used to describe solute transport in this system:

\[ \frac{\partial c_\omega}{\partial t} = \nabla \cdot (D_\omega (r) \nabla c_\omega), \quad \text{in } \mathcal{V}_\omega, \] (1)

\[ n_{\omega \kappa} \cdot (D_\omega (r) \nabla c_\omega) = n_{\omega \kappa} \cdot (D_\kappa \nabla c_\kappa), \quad \text{on } \mathcal{A}_{\omega \kappa}, \] (2)

\[ c_\omega = c_\kappa, \quad \text{on } \mathcal{A}_{\omega \kappa}, \] (3)

\[ \frac{\partial c_\kappa}{\partial t} + \nabla \cdot (v_\kappa c_\kappa) = \nabla \cdot (D_\kappa \nabla c_\kappa), \quad \text{in } \mathcal{V}_\kappa. \] (4)

In these equations, \( c_\alpha \) is the pointwise concentration (nutrient or antimicrobial agent) in the phase \((\alpha)\) with \((\alpha = \omega, \kappa)\); \( D_\omega (r) \), also referred to as \( D_\omega \) for simplicity, is the diffusion coefficient field within the cell-EPS phase, \textit{that can be actively modified by the microorganisms}; \( D_\kappa \) is the diffusion coefficient in the channel phase; \( \mathcal{V}_\alpha \) is the open bounded set that represents the \( \alpha \)-phase within the REV; \( \mathcal{A}_{\omega \kappa} \) is the interface between the channel phase and the cell-EPS phase; \( n_{\omega \kappa} \) is the unit vector normal to \( \mathcal{A}_{\omega \kappa} \) pointing from \( \omega \) to \( \kappa \); and \( v_\kappa \) is the velocity field in the fluid phase. We will assume that this velocity field is known pointwise throughout the entire system, in order to focus on mass transport, rather than momentum transport. The reader is referred to [25] for an extensive discussion on fluid flow in biological media.

In Eq (2), we have assumed that the velocity field is null on \( \mathcal{A}_{\omega \kappa} \) so that the interfacial flux across the boundary is purely diffusive. We have also assumed that the system is at thermodynamic equilibrium, and that equality of the chemical potentials on \( \mathcal{A}_{\omega \kappa} \) leads to continuity of the concentrations there. In practice, this purely thermodynamic constraint could be relaxed easily by applying a suitable constitutive law for the chemical potentials. For instance, in diluted cases, this equality is often written in terms of a jump condition for the concentrations, \( c_\omega = K c_\kappa \) on \( \mathcal{A}_{\omega \kappa} \), in which \( K \) is a function of the pressure and the temperature. For the purposes of the upscaling performed in the remainder of this study, the only constraint that is mandatory is that this relationship between \( c_\omega \) and \( c_\kappa \) should be affine. For simplicity, we restrict attention to the case \( c_\omega = c_\kappa \) on \( \mathcal{A}_{\omega \kappa} \), noting that an extension to \( c_\omega = K c_\kappa \) on \( \mathcal{A}_{\omega \kappa} \) would be straightforward, using a simple change of variables.

### III. PERTURBATION ANALYSIS

In this section, the transport equation in each phase is averaged in space (as defined in Fig 1), and the pointwise fields are decomposed into an averaged part plus a perturbation.
The averaged component is allowed to vary on a characteristic length $R$, while the perturbation varies with a characteristic length $l_\kappa$, where we assume $R \gg l_\kappa$ in order to perform an asymptotic analysis.

**A. Definitions**

First, we define the volume of the phase ($\alpha = \omega, \kappa$), $V_\alpha = \int_{V_\alpha} dV$, and the total volume of the REV, $V = V_\omega + V_\kappa$. We introduce the superficial average of any tensor field, $\pi_\alpha$, (for tensors of order 0, 1 or 2) by $\langle \pi_\alpha \rangle = \frac{1}{V_\alpha} \int_{V_\alpha} \pi_\alpha dV$. We define the volume fraction (which we take to be constant throughout the biofilm) of the $\alpha$-phase, $\varepsilon_\alpha = \frac{V_\alpha}{V}$, and the intrinsic average, $\langle \pi_\alpha \rangle^\alpha = \frac{1}{\varepsilon_\alpha} \langle \pi_\alpha \rangle$. We will perform a perturbation analysis by considering decompositions of the form:

$$\pi_\alpha = \langle \pi_\alpha \rangle^\alpha + \tilde{\pi}_\alpha.$$  \hspace{1cm} (5)

where we will assume

$$\frac{\|\tilde{\pi}_\alpha\|_F}{\|\langle \pi_\alpha \rangle^\alpha\|_F} \ll 1$$  \hspace{1cm} (6)

where $\|\cdot\|_F$ is the Frobenius norm (we remark that the metric used is not really important for our purposes because our analysis is essentially based on order of magnitude estimates).

The volume average definitions stated above are general in form, and may be used in several ways. For example, in Fig 1, we depict two different averaging volumes. Determining the most relevant averaging volume is highly specific to the configuration, depending on the properties of the biofilm and the flow, and on the degree of complexity and precision required.

**B. Averaged equations**

Transport equations (1) and (4) are averaged in space to obtain a biofilm-scale description of the system. A brief description can be given as follows. Firstly, integrals of derivatives are expressed as derivatives of integrals plus surface terms by exploiting general transport and spatial averaging theorems [21]. Secondly, we use the decomposition specified by Eq (5), along with the assumed separation of scales, $l_\kappa \ll R \ll L$, to eliminate non-local terms, i.e, integrals that cannot be calculated locally on the representative volume. Some guidelines are given in Appendix A, and detailed descriptions can be found in [35, 54]. In this way, we arrive at the following system of macroscopic equations for $\langle c_\omega \rangle^\omega$ and $\langle c_\kappa \rangle^\kappa$:

\hspace{1cm}
\[ \varepsilon_\omega \frac{\partial \langle c_\omega \rangle^\omega}{\partial t} - \left( \frac{1}{V} \int_{A_\omega} \mathbf{n}_{\omega n} D_\omega dA \right) \cdot \nabla \langle c_\omega \rangle^\omega \]

\[ = \varepsilon_\omega \nabla \cdot \left[ (D_\omega)^\omega \left( \nabla \langle c_\omega \rangle^\omega + \frac{1}{V_\omega} \int_{A_\omega} \mathbf{n}_{\omega n} \tilde{c}_\omega dA \right) \right] \]

\[ + \frac{1}{V} \int_{A_\omega} \mathbf{n}_{\omega n} \cdot (D_\omega \nabla \tilde{c}_\omega) \, dA + \varepsilon_\omega \nabla \cdot (\tilde{D}_\omega \nabla \tilde{c}_\omega)^\omega, \]  

(7)

\[ \varepsilon_\kappa \frac{\partial \langle c_\kappa \rangle^\kappa}{\partial t} + \varepsilon_\kappa \langle \mathbf{v}_\kappa \rangle^\kappa \cdot \nabla \langle \tilde{c}_\kappa \rangle^\kappa \]

\[ = \varepsilon_\kappa \nabla \cdot \left[ D_\kappa \left( \nabla \langle c_\kappa \rangle^\kappa + \frac{1}{V_\kappa} \int_{A_\kappa} \mathbf{n}_{\kappa n} \tilde{c}_\kappa dA \right) \right] \]

\[ + \frac{1}{V} \int_{A_\kappa} \mathbf{n}_{\kappa n} \cdot (D_\kappa \nabla \tilde{c}_\kappa) \, dA - \varepsilon_\kappa \nabla \cdot (\tilde{v}_\kappa \tilde{c}_\kappa). \]  

(8)

We remark that Eqs (7) and (8) contain integrals which contain correction terms to the average concentrations. To close the problem and obtain a macroscopic formulation for \( \langle c_\alpha \rangle^\alpha \) (\( \alpha = \omega, \kappa \)), it remains to express \( \tilde{c}_\alpha \) as a function of \( \langle c_\alpha \rangle^\alpha \) and its derivatives. This is done in two steps. First, the boundary-value-problem governing the perturbations is derived. Second, a careful analysis in terms of Green’s functions yields a suitable closure.

C. Perturbations

Since \( \tilde{\pi}_\alpha = \pi_\alpha - \langle \pi_\alpha \rangle^\alpha \), equations for the perturbations can be obtained by subtracting suitable multiples of Eqs (7) and (8) from Eqs (1) and (4), respectively. In addition, we may neglect derivatives of averaged quantities because, in the continuum limit, the REV can be treated as a “macroscopic point”, i.e., there is a separation of the length scales \( R \ll L \) (cf. detailed discussions in [54]). In the general case, the fluctuations satisfy a transient problem and the homogenized equations contain time-convolutions (e.g., in [31]). Such a formulation is useful for describing short time phenomena and accounts for time non-locality. Since these short-time phenomena are not relevant for our biofilm application, we will consider only a steady-state problem for the fluctuations. This hypothesis is standard and is generally referred to as the quasi-stationarity of the perturbation problem [54].
The result of this procedure can be written, in the phase ($\omega$), as:

\[
\left(\langle \nabla D \rangle^\omega \cdot \nabla \langle c^\omega \rangle^\omega - \nabla \nabla \langle c^\omega \rangle^\omega\right) = \nabla \cdot \left(\langle \nabla \cdot (D \nabla \tilde{c}^\omega)\rangle^\omega \right), \text{ in } \mathcal{V}_\omega.
\] (9)

The boundary conditions are:

\[
n_{\omega\kappa} \cdot \left(D \nabla \langle c^\omega \rangle^\omega - D \nabla \langle c^\kappa \rangle^\kappa\right) = \nabla \cdot \left(D \nabla \tilde{c}^\kappa - D \nabla \tilde{c}^\omega\right), \text{ on } \mathcal{A}_{\omega\kappa}, \] (10)

and

\[
\langle c^\omega \rangle^\omega - \langle c^\kappa \rangle^\kappa = \tilde{c}^\kappa - \tilde{c}^\omega, \text{ on } \mathcal{A}_{\omega\kappa}. \] (11)

In the phase ($\kappa$), we have:

\[
\nabla \cdot \left(D \nabla \langle c^\kappa \rangle^\kappa \right) - \langle \nabla \cdot (D \nabla \tilde{c}^\kappa)\rangle^\kappa = \nabla \cdot \left(D \nabla \langle c^\kappa \rangle^\kappa \right), \text{ in } \mathcal{V}_\kappa.
\] (12)

Eqs (9) to (12) are coupled to Eqs (4) and (7) and need to be reformulated to facilitate solution. Our goal is to separate the contributions that act on the microscopic level from those that act on the macroscopic level. The first step is to identify the three different macroscopic source terms in these equations: $\nabla \langle c^\omega \rangle^\omega$, $\nabla \langle c^\kappa \rangle^\kappa$ and $\langle c^\omega \rangle^\omega - \langle c^\kappa \rangle^\kappa$. Since Eqs (9) to (12) are linear in $\tilde{c}$, they can be written as $\mathcal{L} (\tilde{c}) = \mathcal{S}_V (\nabla \langle c^\omega \rangle^\omega, \nabla \langle c^\kappa \rangle^\kappa)$, and $\mathcal{B} (\tilde{c}) = \mathcal{S}_A (\nabla \langle c^\omega \rangle^\omega, \nabla \langle c^\kappa \rangle^\kappa, \langle c^\omega \rangle^\omega - \langle c^\kappa \rangle^\kappa)$ respectively, in which $\tilde{c} = (\tilde{c}^\kappa, \tilde{c}^\omega)$. $\mathcal{L}$ is the linear operator defined in the bulk phases, $\mathcal{B}$ the linear operator representing the boundary conditions and $\mathcal{S}_V$, $\mathcal{S}_A$ are the corresponding source terms. By invoking the superposition principle for this boundary value problem, a solution can be separated in three components, each corresponding to one of the source terms. Again recall that we are interested in the continuum limit $R \ll L$, so that these sources can be considered as constant forcing terms and the solution may be written:

\[
\tilde{c}_\alpha = b_{\alpha\kappa} \cdot \nabla \langle c^\kappa \rangle^\kappa + b_{\alpha\omega} \cdot \nabla \langle c^\omega \rangle^\omega + s_\alpha (\langle c^\omega \rangle^\omega - \langle c^\kappa \rangle^\kappa),
\] (13)

with $\alpha = \omega$ or $\kappa$.

A different analysis may be carried out by using Green’s functions (cf. [55]) and this yields a similar expression for the perturbations. In this case, the solution is decomposed.
into components corresponding to the different source terms. The perturbations are then expressed as integrals of the Green’s functions and the source terms, over the spatial variable $x'$ that fixes the position of the Dirac’s distributions. In the continuum limit $R \ll L$, we can extract the sources $\nabla \langle c_\kappa \rangle^\kappa$, $\nabla \langle c_\omega \rangle^\omega$ and $\langle c_\omega \rangle^\omega - \langle c_\kappa \rangle^\kappa$ from the integrals and treat these as constant over the lengthscale of the REV. Therefore, the mapping variables $b_{\alpha \beta}$ and $s_\alpha$ can also be interpreted as integrals of the corresponding Green’s functions over $x'$.

Substituting Eq (13) into Eqs (9) to (12) and collecting terms involving $\nabla \langle c_\kappa \rangle^\kappa$, $\nabla \langle c_\omega \rangle^\omega$ and $\langle c_\omega \rangle^\omega - \langle c_\kappa \rangle^\kappa$ leads to three boundary value problems (given in Appendix B) that govern $b_{\alpha \kappa}$, $b_{\alpha \omega}$ and $s_\alpha$. These problems are generally solved over a representative portion of the medium, termed the unit cell, for which periodic conditions are often used on the boundary between the unit cell and the rest of the system. The last step of this process is to ensure uniqueness of the solution to Eq (13), and of the mapping fields. To do this, we fix $\langle b_{\alpha \kappa} \rangle^\alpha = \langle b_{\alpha \omega} \rangle^\alpha = 0$ and $\langle s_\alpha \rangle^\alpha = 0$ to ensure that $\langle \tilde{c}_\alpha \rangle^\alpha = 0$.

IV. CLOSED MACROSCOPIC FORMULATIONS

Now that we have obtained explicit expressions for the perturbations, we can return to Eqs (7) and (8) and obtain a closed form for these macroscopic equations.

A. The two-equation model

Substituting Eq (13) in Eqs (7) and (8) leads to:

$$
\varepsilon_\kappa \frac{\partial \langle c_\kappa \rangle^\kappa}{\partial t} + \varepsilon_\kappa \sum_{\alpha = \omega, \kappa} \nabla \cdot (V_{\kappa \alpha} \langle c_\alpha \rangle^\alpha) = \varepsilon_\kappa \sum_{\alpha = \omega, \kappa} \nabla \cdot (D_{\kappa \alpha} \cdot \nabla \langle c_\beta \rangle^\beta) - h \left( \langle c_\kappa \rangle^\kappa - \langle c_\omega \rangle^\omega \right),
$$

(14)

$$
\varepsilon_\omega \frac{\partial \langle c_\omega \rangle^\omega}{\partial t} + \varepsilon_\omega \sum_{\alpha = \omega, \kappa} \nabla \cdot (V_{\omega \alpha} \langle c_\alpha \rangle^\alpha) = \varepsilon_\omega \sum_{\alpha = \omega, \kappa} \nabla \cdot (D_{\omega \alpha} \cdot \nabla \langle c_\beta \rangle^\beta) - h \left( \langle c_\omega \rangle^\omega - \langle c_\kappa \rangle^\kappa \right).
$$

(15)

In Eq (15), the effective parameters $V_{\alpha \beta}$, $D_{\alpha \beta}$ and $h$ can be expressed explicitly as integrals
of the mapping fields over the unit cell. For the velocities, we have:

\[
V_{\alpha\beta} = -\frac{1}{V}\int_{A_w} \mathbf{n}_\alpha \cdot [D_\alpha (\nabla b_{\alpha\beta} + (\delta_{\alpha\omega} - \delta_{\alpha\kappa}) s_\alpha \mathbf{l})] \, dA \\
- \frac{1}{V}\int_{A_w} \mathbf{n}_\alpha \cdot (D_\alpha \delta_{\alpha\beta}) \, dA + \delta_{\alpha\beta} \langle \mathbf{v}_\alpha \rangle^\alpha.
\] (16)

For the dispersion tensors, we obtain:

\[
D_{\alpha\beta} = \langle D_\alpha (\delta_{\alpha\beta} \mathbf{l} + \nabla b_{\alpha\beta} + (\delta_{\alpha\omega} - \delta_{\alpha\kappa}) s_\alpha \mathbf{l}) \rangle^\alpha \\
- \delta_{\alpha\beta} \langle \tilde{\mathbf{v}}_\alpha b_{\alpha\beta} \rangle^\alpha.
\] (17)

The mass exchange coefficient is:

\[
h = -\frac{1}{V}\int_{A_w} \mathbf{n}_{\omega\kappa} \cdot (D_\omega (r) \nabla s_\omega) \, dA \\
= \frac{1}{V}\int_{A_w} \mathbf{n}_{\omega\kappa} \cdot (D_\omega \nabla s_\kappa).
\] (18)

In these equations, we have used \(\delta_{\alpha\beta} = 1\) if \(\alpha = \beta\), \(\delta_{\alpha\beta} = 0\) if \(\alpha \neq \beta\). Here, we have assumed, for simplicity, that these effective properties are constant through the biofilm, so that Eqs (14) and (15) can be written in a conservative or non-conservative form.

These kind of upscaling approaches, in which the effective parameters are calculated on a representative portion of the system, are becoming increasingly relevant considering recent progresses in imaging techniques such as OCT, CLSM or X-ray microtomography. Instead of determining only volume fractions, porosities or densities, we can calculate numerically the effective parameters relevant to our specific application by directly using the images obtained.

Physically, Eqs (14) and (15) mean that we have a continuous macroscopic transport equation for each phase (dual-continua description), in which mass is exchanged with a characteristic time \(h^{-1}\). Similar models have been used to describe mass transport in highly heterogeneous porous media [5] and heat transfer problems [34]. Eqs (14) and (15) can be used to describe a broad range of non-Fickian transport phenomena, for which \(h^{-1}\) is large compared to other characteristic timescales associated with transport mechanisms. Such situations may arise when the microorganisms actively alter the penetration of the solute or expel it from the cell clusters. We also remark that our model equations are quite general, in that they are not geometry-specific, and the phases are arbitrary. For example, upon including the bulk water phase in the definition of the channels and imposing a relevant
separation of length scales, our model may also be adapted to describe non-Fickian transport phenomena induced by biofilm growth in porous media.

B. Telegrapher’s equations

On neglecting higher order spatial derivatives, it is possible to approximate Eqs (14) and (15) by a variant of the telegrapher’s equation. This may be written (see Appendix C for details):

\[
\frac{\varepsilon_\kappa \varepsilon_\omega}{h} \frac{\partial^2}{\partial t^2} \cdot \mathbf{v}_e \cdot \nabla \cdot \mathbf{v}_e - \nabla \cdot \left( \mathbf{D}^* \cdot \nabla \cdot \mathbf{v}_e \right) \langle c \rangle_{\omega\kappa}
\]

\[
+ \left[ \frac{\varepsilon_\kappa \varepsilon_\omega}{h} (\mathbf{V}_{\kappa\kappa} + \mathbf{V}_{\omega\omega}) \cdot \nabla \cdot \mathbf{v}_e \right] \langle c \rangle_{\omega\kappa}
\]

\[
- \left\{ \frac{\varepsilon_\kappa \varepsilon_\omega}{h} \nabla \cdot \left[ (\mathbf{D}_{\kappa\kappa} + \mathbf{D}_{\omega\omega}) \cdot \nabla \cdot \mathbf{v}_e \right] \right\} \langle c \rangle_{\omega\kappa} = 0.
\]  

(19)

where

\[
\mathbf{D}^* = \sum_{\alpha=\omega,\kappa} \varepsilon_\alpha (\mathbf{D}_{\alpha\omega} + \mathbf{D}_{\alpha\kappa}) - \frac{\varepsilon_\kappa \varepsilon_\omega}{h} [\mathbf{V}_{\omega\omega} \mathbf{V}_{\kappa\kappa} - \mathbf{V}_{\omega\kappa} \mathbf{V}_{\kappa\omega}],
\]

(20)

and

\[
\mathbf{V}_e = \sum_{\alpha=\omega,\kappa} \varepsilon_\alpha (\mathbf{V}_{\alpha\omega} + \mathbf{V}_{\alpha\kappa}) = \varepsilon_\kappa \langle \mathbf{v}_\kappa \rangle_{\kappa},
\]

(21)

and

\[
\langle c \rangle_{\omega\kappa} = \varepsilon_\omega \langle c_\omega \rangle_{\omega} + \varepsilon_\kappa \langle c_\kappa \rangle_{\kappa}.
\]

(22)

This form of the telegrapher’s equation, Eq (19), is not standard because it contains mixed time-space derivatives. However, upon considering the moving frame \( \mathbf{\bar{r}} = \mathbf{r} - \mathbf{V}_e t \), in order to keep the same asymptotic behaviour, and then neglecting mixed time-space derivatives, we can obtain the classical telegrapher’s equation (see Appendix C for details):

\[
\frac{\varepsilon_\kappa \varepsilon_\omega}{h} \frac{\partial^2}{\partial t^2} \langle c \rangle_{\omega\kappa} + \frac{\partial \langle c \rangle_{\omega\kappa}}{\partial t} = \nabla_{\mathbf{\bar{r}}} \cdot (\mathbf{D}_e \cdot \nabla_{\mathbf{\bar{r}}} \langle c \rangle_{\omega\kappa}),
\]

(23)

with

\[
\mathbf{D}_e = \sum_{\alpha=\omega,\kappa} \varepsilon_\alpha (\mathbf{D}_{\alpha\omega} + \mathbf{D}_{\alpha\kappa})
\]

\[
- \frac{\varepsilon_\kappa \varepsilon_\omega}{h} [\mathbf{V}_{\omega\omega} (\mathbf{V}_{\kappa\kappa} - \mathbf{V}_e) - \mathbf{V}_{\omega\kappa} \mathbf{V}_{\kappa\omega}].
\]

(24)
Eq (23) can be interpreted as a wave equation ($\partial_{tt}$ dominated) with a perturbation ($\partial_t$) that disappears at early times, or as a diffusion equation ($\partial_t$ dominated) with a wave perturbation ($\partial_{tt}$) that disappears in the long-time limit [45, 52]. Note that the wave-like behaviour at early times is physically unrealistic for our application because the assumption of quasi-stationarity of the perturbation problem is not valid in the short-time limit, when non-local effects must be considered.

In the mathematical derivation presented in Appendix C, higher order and mixed space/time derivatives represent a deviation from the classical telegrapher’s model. Higher order terms must be eliminated in order to be consistent with the first order closure on the perturbations, Eq (13), performed during upscaling. However, the influence of the mixed space/time derivatives upon the solutions is not straightforward, and a complete form, Eq (19), may be needed in some cases. Such models, containing mixed derivatives, have been discussed previously in [39, 47, 50] in the case of two-phase heat conduction, where it is also known as dual-phase-lagging heat conduction models, or in [39] for solute contaminant transport. Future work should focus on understanding the exact mathematical relationship between Eqs (19) and (23), for different choices of boundary conditions, initial conditions, parameters and geometries; and compare numerical simulations with experimental results in order to determine the exact effect of the mixed time-space derivatives.

The operators derived in Appendix C also apply to each intrinsic average concentration and, when mixed time-space derivatives can be neglected, an approximation of Eq (15) can be described in terms of two telegrapher’s equations, one for each phase:

\[
\frac{\varepsilon_\kappa \varepsilon_\omega}{h} \frac{\partial^2 \langle c_\alpha \rangle^\alpha}{\partial t^2} + \frac{\partial \langle c_\alpha \rangle^\alpha}{\partial t} = \nabla \bar{r} \cdot (D \cdot \nabla \langle c_\alpha \rangle^\alpha), \quad \text{for } \alpha = \omega, \kappa.
\]  

(25)

In Eq (25), boundary conditions, initial conditions (potentially with $\partial_t \langle c_\alpha \rangle^\alpha |_{t=0} \neq 0$) or volume source terms can be tuned individually for each phase, as opposed to Eq (23) where these conditions are imposed on the weighted average concentration. Obviously, the drawback of this formulation, as compared to Eq (23), is that it requires the solution of two equations rather than one. The drawback of both telegrapher’s models, as compared to Eqs (14) and (15), is also that additional initial conditions for the time derivatives of averaged concentrations are required.
C. Time-asymptotic behaviour

For $t \gg \frac{h}{\varepsilon \kappa}$, Eqs (15) is known, at least in the case of a semi-infinite homogeneous medium, to reduce to a single advection-dispersion equation [8, 57]:

$$\frac{\partial \langle c \rangle^{\omega \kappa}}{\partial t} + \mathbf{V}_e \cdot \nabla \langle c \rangle^{\omega \kappa} = \nabla \cdot (D_e \cdot \nabla \langle c \rangle^{\omega \kappa}).$$

(26)

Heterogeneities or the effects of boundary condition may trigger a departure from the asymptotic situation, as has been illustrated in [7]. For the variant of the telegrapher’s model, a similar analysis, e.g., in terms of spatial moments could be used to show that Eq (19) has an asymptotic behaviour that can be described by Eq (26). However, this is straightforward in the moving frame, i.e., by considering the asymptotic behaviour of Eq (23), and then switching back to the static frame.

The dispersion tensor, Eq (20), can be decomposed into three components by substituting the expressions for $D_{\alpha \beta}$ ($\alpha, \beta = \omega, \kappa$), Eq (17), in Eq (24). In this way, we arrive at the following expression for the dispersion tensor (see also [33]):

$$D_e = \sum_{\alpha,\beta=\omega,\kappa} \varepsilon_{\alpha} \langle D_{\alpha} (\delta_{\alpha\beta}l + \nabla b_{\alpha\beta}) \rangle^{\alpha}$$

Averaged diffusion coefficients and tortuosity

$$- \varepsilon_{\kappa} \langle \mathbf{V}_{\kappa} (b_{\kappa\kappa} + b_{\kappa\omega}) \rangle^{\kappa}$$

Hydrodynamic dispersion

$$- \frac{\varepsilon_{\omega} \varepsilon_{\kappa}}{h} \left[ (\mathbf{V}_{\omega \omega} - \mathbf{V}_e) (\mathbf{V}_{\kappa \kappa} - \mathbf{V}_e) - \mathbf{V}_{\omega \kappa} \mathbf{V}_{\kappa \omega} \right].$$

(27)

This expression highlights the notion of effective diffusion that was mentioned in the introduction of this paper. In addition to terms relating to tortuosity and hydrodynamic dispersion, the tensor contains a term specific to the multiphase configuration, that involves $\mathbf{V}_{\alpha \beta}$ ($\alpha, \beta = \omega, \kappa$) given in Eqs (16). This represents a fundamental difference with the expression for the dispersion given in [1], where the assumption of local mass equilibrium results in the absence of multiphase dispersion. The influence of the hydrodynamic and multiphase dispersion terms depends on the situation. If there is marked variation in the mean velocities, for example if the channels have a clear preferred orientation, then the multiphase dispersion term may significantly contribute to the net dispersion effects. However, if the
Figure 2. Illustrations of the telegrapher’s and advection-dispersion fundamental solutions for 
\( \langle c \rangle^{\omega \kappa} (\bar{x}, t = 0) = \delta (\bar{x}) \), \( \partial_t \langle c \rangle^{\omega \kappa} (\bar{x}, t = 0) = 0 \), \( T = 1 \text{ s} \) and \( D_e = 1 \text{ m}^2 \cdot \text{s}^{-1} \): (a) Plot of \( \langle c \rangle^{\omega \kappa}_{\text{tel}} \) (Telegraph), Eq (28), and \( \langle c \rangle^{\omega \kappa}_{\text{asy}} \) (Gaussian), Eq (29). Each curve represents the solution at a given time. Notice that the front, in the telegrapher’s solution, involves a Dirac distribution; (b) Plot showing how the difference \( \langle c \rangle^{\omega \kappa}_{\text{asy}} - \langle c \rangle^{\omega \kappa}_{\text{tel}} \) between the fundamental solutions evolves over time. The telegrapher’s equation can be interpreted as an advection-dispersion equation with a wave perturbation that disappears in the long time limit.

Averaged velocity is small, for example if the channels have no preferred orientation, then the hydrodynamic dispersion originating from velocity fluctuations will become dominant. We remark further that the effective diffusion is usually characterised by a tensor and can only be described by a scalar when the biofilm is isotropic.

V. ANALYTICAL AND NUMERICAL RESULTS

A. Asymptotic behaviour of the telegrapher’s equation

It is important to realise that, although an advection-dispersion equation such as Eq (26) may seem more familiar than Eq (19), there are a number of aspects that make it less pertinent from a theoretical point of view. One important unphysical feature of Eq (26) is
that, unlike Eq (23), its solutions can propagate with infinite speed. Further, since there is no characteristic time associated with mass exchange in Eq (26), it is only valid when mass exchange can be neglected at the macroscale. Therefore, it is important to understand how the telegrapher’s equations and the asymptotic models are related. This can be illustrated by recalling that a fundamental solution to Eq (26) for a one-dimensional cartesian geometry on an infinite domain, with \( \langle c \rangle^\omega (\bar{x}, t = 0) = \delta (\bar{x}) \), is given by:

\[
\langle c \rangle^\omega_{\text{asy}} = \Theta (t) \sqrt{\frac{1}{4 \pi D_e t}} e^{-\frac{\bar{x}^2}{4 D_e t}}.
\]  

(28)

where \( \Theta \) is the Heaviside step function. Similarly, a well-known fundamental solution to Eq (23) posed on a one-dimensional cartesian geometry on an infinite domain, with \( \langle c \rangle^\kappa (\bar{x}, t = 0) = \delta (\bar{x}) \) and \( \partial_t \langle c \rangle^\kappa |_{t=0} = 0 \), is given (e.g., [17]) by:

\[
\langle c \rangle^\kappa_{\text{tel}} = e^{-\frac{\bar{x}^2}{4 T}} \left[ \delta (\bar{x} - \nu t) + \delta (\bar{x} + \nu t) \right] \\
+ e^{-\frac{\bar{x}^2}{4 T}} \left[ \frac{1}{2 \nu T} \left( I_0 (\rho) + t \frac{I_1 (\rho)}{2 T} \right) \Theta (\nu t - |\bar{x}|) \right],
\]  

(29)

where \( \nu = \sqrt{D_e R / \epsilon^\kappa} \), \( T = \epsilon^\omega / \rho \), \( \rho = \sqrt{c^2 - \bar{x}^2 / 2 \epsilon^\kappa} \), \( I_n \) are modified Bessel functions of the first kind.

In Fig 2 (a), we present results showing how these solutions evolve over time and, in Fig 2 (b), we plot their difference, \( \langle c \rangle^\omega_{\text{asy}} - \langle c \rangle^\kappa_{\text{tel}} \). These figures demonstrate that at long times the telegrapher’s equation can be well approximated by the asymptotic model. Standardized moments (especially skewness and kurtosis) can also be used to study the convergence from the two-equation/telegrapher’s model towards Eq (26) (cf. discussions in [8]).

B. Illustration of the multiphase dispersion effect

To understand further the physical significance of the dispersion terms appearing in Eq (27), it is helpful to consider the simple axisymmetric configuration of a tube of radius \( R_1 \), in which \((r, z)\) represent the radial and axial coordinates. The phase \((\kappa)\) occupies the region \( 0 < r < R_0 \) and the phase \((\omega)\) occupies \( R_0 < r < R_1 \). We impose a Poiseuille flow in the phase \((\kappa)\) described by the velocity \( \mathbf{v} = v_0 (1 - r^2 / R_0^2) \mathbf{e}_z \), and suppose that \( D_\kappa = D_\omega = D \) is constant through space. All coefficients of the dispersion tensor, Eq (27), corresponding to a concentration surface-averaged over the width of the tube, vanish except for its axial
Figure 3. Relative dispersion $D_{e}^{zz}/D$ as a function of $Pe$ for $b/hR_{0}^{2} = 1$, $\varepsilon_{\kappa} = 0.0$, $\varepsilon_{\kappa} = 0.1$ (○) and $\varepsilon_{\kappa} = 0.2$ (△). The corresponding Taylor’s dispersion $(1 + Pe^{2}\varepsilon_{\kappa}/48)$ is also presented to highlight the contribution of the multiphase dispersion term.

Component $D_{e}^{zz}$ which can be written as:

$$D_{e}^{zz} = D - \varepsilon_{\kappa} \left( \langle \tilde{v}_{\kappa} (b_{\kappa\kappa} + b_{\omega\omega}) \rangle^{zz}_{\kappa} \right) + \frac{\varepsilon_{\kappa}\varepsilon_{\omega}}{h} \left[ \varepsilon_{\kappa}\varepsilon_{\omega} (V_{\kappa\kappa}^{z} - V_{\omega\omega}^{z})^{2} + V_{\omega\kappa}^{z} V_{\kappa\omega}^{z} \right].$$

(30)

An approximation of $\langle [\tilde{v}_{\kappa} (b_{\kappa\kappa} + b_{\omega\omega})]^{zz}_{\kappa} \rangle$ is simply Taylor’s dispersion, $-1/D \langle [\tilde{v}_{\kappa} (b_{\kappa\kappa} + b_{\omega\omega})]^{zz}_{\kappa} \rangle \approx Pe^{2}/48$, with

$$Pe = \langle v_{0} (1 - r^{2}/R_{0}^{2}) \rangle^{\kappa} R_{0}/b.$$  

(31)

In addition, we assume:

$$V_{\kappa\kappa}^{z} \approx \left( v_{0} \left( 1 - \frac{r^{2}}{R_{0}^{2}} \right) \right)^{\kappa} \gg V_{\omega\omega}^{z}, V_{\omega\kappa}^{z}, V_{\kappa\omega}^{z}.$$  

(32)

Eq (32) means that we are only considering the physical velocity, and neglect velocity-like terms (such as $V_{\omega\kappa}$ or $V_{\kappa\omega}$) that appear during upscaling, but do not correspond to the average pointwise velocity $\langle v_{0} (1 - r^{2}/R_{0}^{2}) \rangle^{\kappa}$. Using Eq (32), we obtain:

$$\frac{\varepsilon_{\kappa}\varepsilon_{\omega}}{h} \left[ \varepsilon_{\kappa}\varepsilon_{\omega} (V_{\kappa\kappa}^{z} - V_{\omega\omega}^{z})^{2} + V_{\omega\kappa}^{z} V_{\kappa\omega}^{z} \right] \approx \frac{\varepsilon_{\kappa}^{2}\varepsilon_{\omega}^{2} D^{2} Pe^{2}}{h R_{0}^{2}}.$$  

(33)

The dispersion coefficient can then be written as:

$$\frac{D_{e}^{zz}}{D} \approx 1 + Pe^{2} \left( \frac{\varepsilon_{\kappa}}{48} + \frac{\varepsilon_{\kappa}^{2}\varepsilon_{\omega}^{2} D}{h R_{0}^{2}} \right).$$

(34)

Illustrations of this expression for the dispersion are given in Fig 3. Note that in this case we have $D_{e}^{zz}/D \geq 1$, for all values of $Pe$, because $D_{\kappa} = D_{\omega} = D$ and $h$ does not depend on $Pe$. 

21
From Eq (34) and Fig 3, we see that the multiphase term acts as a correction to the classical hydrodynamic dispersion. Taylor’s dispersion arises because of the velocity perturbation within the $\kappa$-phase, while the multiphase term is a consequence of differences between the mean velocities within each phase. This also suggests that the multiphase dispersion term makes a significant contribution to the net dispersion, in cases for which the averaged velocity is relatively large. It is also worth noting that the dispersion coefficient still exhibits $Pe^2$ dependence, but with a different coefficient of proportionality.

C. Longitudinal dispersion in a simple unit cell

In this section, our goal is to illustrate the behaviour of the longitudinal component of the dispersion tensor, $D_{\varepsilon}^{xx}$, in a simple 2-D geometry, as described in Fig 4. To compute $D_{\varepsilon}^{xx}$, we could solve numerically the closure problems presented in Appendix B, and use Eq (27). However, the dispersion tensor may also be written in a more suitable way for computational purposes (see Davit, Quintard and Debenest [10] for details):

$$\frac{D_{\varepsilon}^{xx}}{D_{\kappa}} = \varepsilon_{\kappa} \left[ (I + \langle \nabla B'_{\kappa} \rangle)^{\kappa} - Pe \langle v'_{\kappa} B'_{\kappa} \rangle^{\kappa} \right] + \varepsilon_{\omega} \left[ D_{\Gamma} (I + \langle \nabla B'_{\omega} \rangle)^{\omega} \right],$$

(35)
Figure 5. Solutions of the closure problem for the $x$-component of $B'_\omega$. Results were computed using COMSOL Multiphysics 4.2 (PARDISO solver).

Figure 6. Logarithmic plots of $\frac{D_x}{D_\kappa}$ as a function of $Pe$ for different values of $D_\Gamma$. Calculations were performed using COMSOL Multiphysics 4.2 and the geometry presented in Fig 4. This figure shows the complex non-linear dependence of effective diffusion coefficients upon the system of parameters. For $Pe \ll 1$, transport is diffusion-dominated. For $Pe \geq 10$, hydrodynamic and multiphase dispersion effects become dominant.
where \( L \) is a characteristic length, \( B'_{\alpha} = B_{\alpha}/L \), \( Pe = \sqrt{\langle v_\kappa \rangle^{\omega} \langle v_\kappa \rangle^{\kappa}}/L/b_\kappa \), \( v'_\kappa = v_\kappa/\sqrt{\langle v_\kappa \rangle^{\omega} \langle v_\kappa \rangle^{\kappa}} \) and \( D_\Gamma = b_\omega/b_\kappa \). \( B'_{\alpha} \) solves the following boundary value problem:

\[
-\varepsilon_\kappa \langle v'_\kappa \rangle^{\kappa} = \nabla \cdot \left( D_\Gamma \frac{Pe}{D_\kappa} \nabla B'_{\omega} \right), \quad & \text{in } \mathcal{V}_\omega, \\
\nabla \cdot (v'_\kappa B'_\kappa) + \tilde{v}'_\kappa + \varepsilon_\omega \langle v'_\kappa \rangle^{\kappa} = \nabla \cdot \left( \frac{1}{Pe} \nabla B'_\kappa \right), \quad & \text{in } \mathcal{V}_\kappa,
\]

with the boundary conditions:

\[
n_{\omega\kappa} \cdot \left( \frac{1}{Pe} \nabla B_\kappa - \frac{D_\Gamma}{Pe} \nabla B'_\omega \right) = -n_{\omega\kappa} \left( \frac{1}{Pe} - \frac{D_\Gamma}{Pe} \right), \quad & \text{on } \mathcal{A}_{\omega\kappa},
\]

and

\[
0 = B'_{\kappa\kappa} - B'_{\omega\kappa}, \quad & \text{on } \mathcal{A}_{\omega\kappa}.
\]

Unicity of the solution is obtained by imposing \( \varepsilon_\omega \langle B'_\omega \rangle^{\omega} + \varepsilon_\kappa \langle B'_\kappa \rangle^{\kappa} = 0 \).

We used COMSOL Multiphysics 4.2 (PARDISO solver) to solve this problem and compute the longitudinal coefficient of the dispersion tensor. The computational mesh is presented in Fig 4, and consisted of triangular meshes (56570 elements). Here, our primary purpose is to capture the qualitative behaviour of the dispersion coefficient. For a more quantitative description, other numerical methods may be necessary, along with a finer mesh in the vicinities of the corners.

Solutions were obtained in the following way. First, the velocity and pressure fields were determined by solving the Stokes equations with periodic boundary conditions and a unit pressure difference along the \( x \)-axis. The resulting velocity field was then used to compute the \( x \)-component of \( B'_\omega \) (see Fig 5). This field was used in Eq (35) to determine \( D'_{xx}/D_\kappa \) for different values of \( D_\Gamma \) and \( Pe \) (see Fig 6). Here, \( D'_{xx} \) is rescaled with \( D_\kappa \) in order to produce results comparable with those of the experimental literature. However, from a theoretical point of view, \( D'_{xx} \) should be rescaled with \( (\varepsilon_\kappa + \varepsilon_\omega D_\Gamma)D_\kappa \) in order to eliminate the effect of \( D_\Gamma \) in the limit when \( Pe \to 0 \).

Our results highlight the complex, non-linear dependence of the dispersion tensor upon the system of parameters. For \( Pe \ll 1 \), transport is diffusion-dominated and only tortuosity affects the longitudinal dispersion coefficient. However, for \( Pe \geq 10 \), hydrodynamic and multiphase dispersion effects become dominant. These results also show that, even for

24
\( Pe \geq 1 \), i.e., in the advection dominated regime, we have a relatively broad range of Péclet numbers for which \( \frac{Pe}{\kappa} \leq 1 \). In other words, \( \frac{Pe}{\kappa} \leq 1 \) does not necessarily imply that transport at the microscale is diffusion dominated.

VI. DISCUSSION

Solute transport in biofilms is often described via a notion of effective diffusion, characterised by the ratio, \( \frac{D_e}{D_{aq}} \), of effective, \( D_e \), and reference, \( D_{aq} = D_\kappa \), diffusion coefficients. As discussed in the introduction, the definition of this effective diffusion coefficient, as reported in the literature, is ambiguous. In order to provide a clearer definition and to obtain physical insight, we have used the technique of volume averaging to derive three classes of models for solute transport. One of these models, Eq (26), is an advection-dispersion equation involving an effective dispersion tensor that can be used to interpret the above notion of effective diffusion. In most cases, this one-equation asymptotic model, Eq (26), is preferable to the other two formulations, i.e., the two-equation and telegrapher’s models. Firstly, it is simple so that it can be easily used to interpret experimental data. Secondly, it has a broad domain of validity, requiring only that a single time inequality is satisfied, \( t \gg \frac{\varepsilon_\kappa \varepsilon_\omega}{h} \), where \( \varepsilon_\alpha \) is the volume fraction of the phase (\( \alpha = \omega, \kappa \)) and \( h \) is the first order mass exchange coefficient of the two-equation model (see section IV C for more details). To appreciate what constraint this inequality poses, consider passive oxygen diffusion in a biofilm of size \( l = 100 - 1000 \mu m \) at temperature 25°C so that \( D = 20 \cdot 10^{-6} \text{ cm}^2 \cdot \text{s}^{-1} \) and suppose that there is a purely diffusive flux at the channel/cluster interface. In this configuration, a good approximation for \( h^{-1} \) is the characteristic time for a molecule of solute to diffuse across the entire width of the biofilm, i.e., \( \frac{l^2}{D} \approx 50 - 500 \text{ ms} \), in which case the previous constraint, for the validity of the one-equation time-asymptotic model, supplies \( t \gg 50 - 500 \text{ ms} \). Therefore, for a typical macroscopic characteristic time of a few seconds or minutes, the constraint is satisfied.

This model also has a straightforward physical interpretation, and each component of the dispersion tensor, Eq (27), can be explicitly identified. Two types of dispersion effects are active. One arises from velocity fluctuations within the channels. The other is due to differences in the mean velocities of the two phases. The consequence of these terms, on a macroscopic level, is the facilitation of solute transport within the biofilm, potentially leading to situations for which \( \frac{D_e}{D_{aq}} > 1 \). Therefore, our analysis provides a solid theoretical
basis that can be used to interpret data for which $D_e/D_{aq} > 1$. In addition, Eq (27) shows that the effective dispersion tensor depends on the geometry of the channels network. This suggests that parameters describing the geometrical properties of these networks, e.g., their connectivity, may be used in empirical laws of $D_e$, in addition to parameters such as the cell density or the charge of the EPS.

Interestingly, and to the best of our knowledge, the effect of the macroscopic advective term $\mathbf{V}_e \cdot \nabla \langle c \rangle^{\omega \kappa}$ has not previously been reported in the literature. One must realize that its effect is extremely difficult to detect, especially on a thin biofilm (typically 100 µm thick). Consider, for example, the simple tube described above in the cases $Pe \gg 1$, and $Pe \ll 1$. A macroscopic Péclet number can be defined by $Pe^M = \frac{v_e R_1}{D_e}$ and can be expressed, using Eqs (34) and (32), as $Pe^M \approx \frac{R_1}{[\rho_0 \rho_e (\varepsilon_0 \varepsilon + \varepsilon_2 \varepsilon_0 \varepsilon_0 \kappa)]} \ll 1$ for $Pe \gg 1$. Similarly, for $Pe \ll 1$, using Eq (34), we have $Pe^M \approx \frac{Pe^{R_1}}{R_0} \ll 1$. This means that, because of the dependence of $D_e$ upon the square of the microscopic Péclet number, the macroscopic advective term may be neglected for both $Pe \gg 1$ and $Pe \ll 1$. We remark also that, for a biofilm thickness $L$ (or $R_1$ in the tube case) which is sufficiently small, the macroscopic advective term may be systematically neglected. Cases for which the advective term may be important correspond to situations in which the channels are oriented parallel to the boundary. In any case, even if this term is negligible, this does not mean that the effects of advection can be neglected when calculating the net dispersion tensor. This result, together with the expression for the dispersion tensor given by Eq (27), suggests that $D_e/D_{aq} < 1$ does not necessarily correspond to diffusion-dominated regime, contrary to what was proposed in [20]. This is also illustrated in Fig 6, where we observe, in a simple unit cell, that $D_e/D_{aq} < 1$ for a broad range of values of the Péclet number with $Pe > 1$ (i.e., in the advection-dominated regime).

Even though the one-equation advection-dispersion model is straightforward and widely applicable, there are some situations for which a two-equation model or a telegrapher’s model may be more appropriate. Microorganisms within biofilms are known to actively restrict the penetration of antimicrobial agents within the cell clusters [12, 27, 49]. For example, positively-charged molecules of antibiotics, such as aminoglycosides, can be bound to negatively charged EPS and have limited permeation properties [12]. More recently, Epstein et al. [14] have revealed the extent to which biofilms can limit the penetration of liquids and gas. They measured the contact angle of liquid drops on a *Bacillus subtilis* biofilm and showed that its surface remains nonwetting against up to 80% aqueous solutions.
of ethanol, surpassing the repellency of Teflon and Lotus leaves. Using X-ray computed tomography, they have shown that this biofilm can also be impenetrable to gas. In another study, Václavová et al. [46] showed that wild yeast biofilms can develop drug resistance “in which specialized cells jointly execute multiple protection strategies”. In particular, their analysis shows that the cells selectively create permeable EPS, while coordinated efflux pumps actively expel toxic substances outside the cell clusters.

These results show that biofilms have the capacity drastically to retard the penetration of antimicrobial agents, and even actively to expel toxic substances. In terms of our modelling approach, this means that the interfacial flux between the channel and cluster phases is modified, for example by reducing $D_\infty$. As a result, the macroscopic mass exchange coefficient, $h$, between the channels and the cell clusters, can be actively controlled by the microorganisms. If $h$ becomes sufficiently small, the dispersion model discussed previously may cease to be valid for any timescale, and the two-equation/telegrapher’s models are needed. Fig 7 illustrates this temporal behaviour. In addition, because we consider abstract phase geometries, these models can be used to describe solute transport in porous media colonized by biofilms. In such systems, biofilms are known substantially to modify mass transport and can be responsible for anomalous behaviours (e.g., in [38]). Our models can be adapted readily to describe such situations, in the limiting case where the phase ($\kappa$) also represents the bulk water phase within the porous matrix and there is separation of the relevant length scales.

To determine whether a two-equation, a telegrapher’s model or a variation of the telegrapher’s model is better suited to biofilms, additional experimental and numerical data are required. Both classes of models can be used to describe non-Fickian transport, both admit a larger range of solutions than the one-equation advection-dispersion model and will provide more flexibility in inverse optimization approaches. In this work, we have shown that telegrapher’s models can be viewed as approximations to the two-equation exchange model. In addition, the telegrapher’s equation has had a recent resurgence in numerous scientific fields and may represent a reasonable compromise between the simplicity of the one-equation model, and the complexity of the two-equation one. It has been used to describe short time phenomena in heat transfer [4, 23] and in other transport problems [52]. Numerical schemes are available to solve this hyperbolic equation, as well as several analytical solutions (e.g., discussions in [52]). We believe that the telegrapher’s equations may be good candidates
Figure 7. Illustration of the domains of validity of the different models presented in this paper. $\tau_1$ is a characteristic time associated with the relaxation of the effective parameters and $\tau_2 = \epsilon \omega / h$. For short time phenomena ($t \ll \tau_1$) the transport is non-local in time and none of the models presented in this study are suitable. The telegrapher’s models exhibit a wave behaviour in this regime, but it is a mathematical artifact that has no physical significance. For times $\tau_1 \ll t \ll \tau_2$, the transport is non-Fickian and two-equation or telegrapher’s models should be used. For $t \gg \tau_2$, the notion of effective diffusion becomes relevant and an advection-dispersion model is sufficient.

for modelling the transport of antimicrobial agents within biofilms and porous media with biofilms, i.e., to describe situations in which advection cannot be neglected within the fluid-channels and the solute has a limited permeation within the cell clusters. Future work will focus on comparing model simulations with experimental data, and characterising the differences between the two-equation and telegrapher’s models.

VII. CONCLUSION

To summarize, in this paper:

1. We have proposed three different, but related, classes of models to describe mass transport within porous biofilms: a two-equation model (see Eq (15)), telegrapher’s models (see Eqs (19), (23) and (25) and Appendix C), and a one-equation time-asymptotic model (see Eq (26)). We have derived these models using the method of volume averaging with closure, have obtained an explicit definition for all the parameters, and have discussed the domain of validity of each model (see illustration in Fig 7). We have also emphasised that future research should explore, mathematically and experimentally, the relationship between the two-equation and telegrapher’s models.

2. We have suggested that the two-equation and telegrapher’s models can be used to describe a broad range of non-Fickian transport phenomena that arise in cases where
the microorganisms actively limit the penetration of biocides within the cell clusters, and also when biofilms colonize porous media.

3. We have studied the concept of effective diffusion and have shown that it corresponds to a diffusion tensor that appears in the one-equation, time-asymptotic formulation. In the case of porous biofilms, this tensor contains a notion of tortuosity, hydrodynamic dispersion and multiphase dispersion. This result is the main contribution of this study and is consistent with recent results in [48] that show extremely complex channel networks within porous biofilms. It also represents a solid theoretical basis for interpreting experimental data for which \( D_e/D_{aq} > 1 \) and suggests that, even in situations for which \( D_e/D_{aq} < 1 \), microscale advective transport may contribute to dispersion.

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APPENDIX A

As previously stated, we will only consider static boundaries. To invert the integral and differential operators, we use the spatial averaging theorems [21]. Upon averaging Eq (1), we obtain:

\[
\varepsilon_\omega \frac{\partial \langle c_\omega \rangle^\omega}{\partial t} = \varepsilon_\omega \nabla \cdot \langle D_\omega \nabla c_\omega \rangle^\omega + \frac{1}{V} \int_{A_\omega} n_{\omega \kappa} \cdot (D_\omega \nabla c_\omega) dA,
\]

(40)

where we have exploited the spatial averaging theorem, \( \langle \nabla \cdot \pi_\alpha \rangle = \varepsilon_\alpha \nabla \cdot \langle \pi_\alpha \rangle + \frac{1}{V} \int_{A_\omega} n_{\omega \kappa} \cdot \pi_\alpha dA \). Then, in order to separate processes occurring over different length scales, we use the spatial decompositions \( D_\omega = \langle D_\omega \rangle^\omega + \tilde{D}_\omega \) and \( c_\omega = \langle c_\omega \rangle^\omega + \tilde{c}_\omega \). For example, the first term on the right hand side reads:

\[
\nabla \cdot \langle D_\omega \nabla c_\omega \rangle^\omega = \nabla \cdot \left[ \langle D_\omega \rangle^\omega \left( \nabla \langle c_\omega \rangle^\omega + \frac{1}{V_\omega} \int_{A_\omega} n_{\omega \kappa} \tilde{c}_\omega dA \right) \right]
+ \nabla \cdot \langle \tilde{D}_\omega \nabla \tilde{c}_\omega \rangle^\omega.
\]

(41)
Other terms, and Eq (4), are treated similarly. For a detailed description of these procedures, the reader is referred to [54].

APPENDIX B

The differential equations governing the mapping variables $b_{\alpha\beta}$ and $s_\alpha$ can be obtained by substituting Eq (13) into Eqs (9) to (12). Using the linearity of the differential and boundary operators, we can collect separately terms involving the three different sources terms $\langle c_\omega \rangle^\omega - \langle c_\kappa \rangle^\kappa$, $\nabla \langle c_\kappa \rangle^\kappa$ and $\nabla \langle c_\omega \rangle^\omega$. In this way, we arrive at the following set of boundary-value-problems:

a. Boundary-value-problem for $s_\alpha$ ($\alpha = \omega, \kappa$), i.e., corresponding to terms involving $\langle c_\omega \rangle^\omega - \langle c_\kappa \rangle^\kappa$

\begin{align}
0 &= \nabla \cdot (D_\omega \nabla s_\omega) - \langle \nabla \cdot (D_\omega \nabla s_\omega) \rangle, \quad \text{in } V_\omega, \tag{42}

0 &= n_{\omega\kappa} \cdot (D_\kappa \nabla s_\kappa - D_\omega \nabla s_\omega), \quad \text{on } A_{\omega\kappa}, \tag{43}

1 &= s_\kappa - s_\omega, \quad \text{on } A_{\omega\kappa}, \tag{44}

\nabla \cdot (v_\kappa s_\kappa) - \langle \nabla \cdot (v_\kappa s_\kappa) \rangle &= \nabla \cdot (D_\kappa \nabla s_\kappa) - \langle \nabla \cdot (D_\kappa \nabla s_\kappa) \rangle^\kappa, \quad \text{in } V_\kappa. \tag{45}
\end{align}

b. Boundary-value-problem for $b_{\alpha\kappa}$ ($\alpha = \omega, \kappa$), i.e., corresponding to terms involving $\nabla \langle c_\kappa \rangle^\kappa$

\begin{align}
\nabla \cdot [D_\omega (\nabla b_{\omega\kappa} - s_\omega)] &= \langle \nabla \cdot [D_\omega (\nabla b_{\omega\kappa} - s_\omega)] \rangle, \quad \text{in } V_\omega, \tag{46}

-n_{\omega\kappa} D_\kappa &= n_{\omega\kappa} \cdot [D_\kappa (\nabla b_{\kappa\kappa} - s_\kappa) - D_\omega (\nabla b_{\omega\kappa} - s_\omega)], \quad \text{on } A_{\omega\kappa}, \tag{47}

0 &= b_{\kappa\kappa} - b_{\omega\kappa}, \quad \text{on } A_{\omega\kappa}, \tag{48}

\nabla \cdot (v_\kappa b_{\kappa\kappa}) - \langle \nabla \cdot (v_\kappa b_{\kappa\kappa}) \rangle + \tilde{v}_\kappa &= \nabla \cdot [D_\kappa (\nabla b_{\kappa\kappa} - s_\kappa)] - \langle \nabla \cdot [D_\kappa (\nabla b_{\kappa\kappa} - s_\kappa)] \rangle^\kappa, \quad \text{in } V_\kappa. \tag{49}
\end{align}
c. Boundary-value-problem for $b_{\omega\kappa}$ ($\alpha = \omega, \kappa$), i.e., corresponding to terms involving $\nabla \langle c_\omega \rangle$.

$$\nabla D_\omega - (\nabla D_\omega)\omega$$

$$= \nabla \cdot [D_\omega (\nabla b_{\omega\omega} + s_\omega)] - (\nabla \cdot [D_\omega (\nabla b_{\omega\omega} + s_\omega)]),$$

in $V_\omega$, \hspace{1cm} (50)

$$n_{\omega\kappa} D_\omega = n_{\omega\kappa} \cdot [D_\kappa (\nabla b_{\kappa\omega} + s_\kappa) - D_\omega (\nabla b_{\omega\omega} + s_\omega)],$$

on $A_{\omega\kappa}$, \hspace{1cm} (51)

$$0 = b_{\kappa\omega} - b_{\omega\omega}, \text{ on } A_{\omega\kappa},$$

(52)

$$\nabla \cdot (v_\kappa b_{\kappa\omega}) - \langle \nabla \cdot (v_\kappa b_{\kappa\omega}) \rangle$$

$$= \nabla \cdot [D_\kappa (\nabla b_{\kappa\omega} + s_\kappa)] - \langle \nabla \cdot [D_\kappa (\nabla b_{\kappa\omega} + s_\kappa)] \rangle \kappa,$$

in $V_\kappa$. \hspace{1cm} (53)

These problems are usually solved only on a representative portion of the system using periodic boundary conditions [54].

### APPENDIX C

The two-equation model Eq (15) can be written using the operator form:

$$L_{\omega\omega} \langle \langle c_\omega \rangle \rangle + L_{\kappa\kappa} \langle \langle c_\kappa \rangle \rangle = 0,$$ \hspace{1cm} (54)

where

$$L_{\alpha\beta} = \delta_{\alpha\beta} \varepsilon_\alpha \frac{\partial}{\partial t} \cdot \varepsilon_\alpha V_{\alpha\beta} \cdot \nabla \cdot - \varepsilon_\alpha \nabla \cdot (D_{\alpha\beta} \cdot \nabla \cdot)$$

$$+ \delta_{\alpha\beta} h \cdot - (1 - \delta_{\alpha\beta}) h \cdot.$$ \hspace{1cm} (55)

Given the linearity of these operators, we can write:

$$(L_{\omega\omega} L_{\kappa\kappa} - L_{\omega\kappa} L_{\kappa\omega}) \langle \langle y \rangle \rangle = 0,$$ \hspace{1cm} (56)
where $\langle y \rangle$ corresponds to either $\langle c_\kappa \rangle^\kappa$, $\langle c_\omega \rangle^\omega$ or $\langle c \rangle^{\omega\kappa}$. On neglecting higher order spatial derivatives, it yields:

$$\left[ \frac{\varepsilon_\kappa \varepsilon_\omega}{h} \frac{\partial^2 \bullet}{\partial t^2} + \frac{\partial \bullet}{\partial t} + \mathbf{V}_e \cdot \nabla \bullet - \nabla \cdot (\mathbf{D}^* \cdot \nabla \bullet) \right] (\langle y \rangle)$$

$$+ \left[ \frac{\varepsilon_\kappa \varepsilon_\omega}{h} (\mathbf{V}_{\kappa \kappa} + \mathbf{V}_{\omega \omega}) \cdot \frac{\partial \nabla \bullet}{\partial t} \right] (\langle y \rangle)$$

$$- \left\{ \frac{\varepsilon_\kappa \varepsilon_\omega}{h} \nabla \cdot \left[ (\mathbf{D}_{\kappa \kappa} + \mathbf{D}_{\omega \omega}) \cdot \frac{\partial \nabla \bullet}{\partial t} \right] \right\} (\langle y \rangle) = 0,$$  \hspace{1cm} (57)

where

$$\mathbf{D}^* = \sum_{\alpha=\omega,\kappa} \varepsilon_\alpha (\mathbf{D}_{\alpha \omega} + \mathbf{D}_{\alpha \kappa}) - \frac{\varepsilon_\kappa \varepsilon_\omega}{h} (\mathbf{V}_{\omega \omega} \mathbf{V}_{\kappa \kappa} - \mathbf{V}_{\omega \kappa} \mathbf{V}_{\kappa \omega}),$$  \hspace{1cm} (58)

and

$$\mathbf{V}_e = \sum_{\alpha=\omega,\kappa} \varepsilon_\alpha (\mathbf{V}_{\alpha \omega} + \mathbf{V}_{\alpha \kappa}).$$  \hspace{1cm} (59)

Upon considering the moving frame $\bar{\mathbf{r}} = \mathbf{r} - \mathbf{V}_e t$, and the change of variables $(\mathbf{r}, t) \rightarrow (\bar{\mathbf{r}}, \tau)$, we have:

$$\frac{\partial}{\partial t} = \frac{\partial}{\partial \tau} - \mathbf{V}_e \cdot \nabla,$$  \hspace{1cm} (60)

and

$$\frac{\partial^2}{\partial t^2} = \left( \frac{\partial}{\partial \tau} - \mathbf{V}_e \cdot \nabla \right) \left( \frac{\partial}{\partial \tau} - \mathbf{V}_e \cdot \nabla \right).$$  \hspace{1cm} (61)

On neglecting the mixed time-space derivatives, we obtain the telegrapher’s equation:

$$\left[ \frac{\varepsilon_\kappa \varepsilon_\omega}{h} \frac{\partial^2 \bullet}{\partial \tau^2} + \frac{\partial \bullet}{\partial \tau} - \nabla_{\bar{\mathbf{r}}} \cdot (\mathbf{D}_e \cdot \nabla_{\bar{\mathbf{r}}} \bullet) \right] (\langle y \rangle) = 0.$$  \hspace{1cm} (62)

with

$$\mathbf{D}_e = \sum_{\alpha=\omega,\kappa} \varepsilon_\alpha (\mathbf{D}_{\alpha \omega} + \mathbf{D}_{\alpha \kappa})$$

$$- \frac{\varepsilon_\kappa \varepsilon_\omega}{h} [(\mathbf{V}_{\omega \omega} - \mathbf{V}_e)(\mathbf{V}_{\kappa \kappa} - \mathbf{V}_e) - \mathbf{V}_{\omega \kappa} \mathbf{V}_{\kappa \omega}].$$  \hspace{1cm} (63)

Note that neglecting the mixed terms may be done only in the moving frame, so that the model still captures the correct asymptotic behaviour.

In the most general case, the mixed derivatives will influence the solutions, and the variation of the telegrapher’s equation, Eq (57), must be considered. However, in some
situations, it may be reasonable to use Eq (62) because: (1) we have already imposed time constraints on the solutions when we have assumed quasi-stationarity of the closure problems (Eqs (9) to (12)), and we may have already neglected similar mixed terms; (2) both models exhibit an identical asymptotic behaviour; (3) both models are used to describe non-Fickian transport phenomena, suggesting that they can yield similar results. Future work should focus on understanding the exact mathematical relationship between these two models, and also compare numerical simulations with experimental results.


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