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New equations for binary gas transport in porous media, Part 1: equation development

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Abstract

A rigorous understanding of the mass and momentum conservation equations for gas transport in porous media is vital for many environmental and industrial applications. We utilize the method of volume averaging to derive Darcy-scale, closure-level coupled equations for mass and momentum conservation. The up-scaled expressions for both the gas-phase advective velocity and the mass transport contain novel terms which may be significant under flow regimes of environmental significance. New terms in the velocity expression arise from the inclusion of a slip boundary condition and closure-level coupling to the mass transport equation. A new term in the mass conservation equation, due to the closure-level coupling, may significantly affect advective transport. Order of magnitude estimates based on the closure equations indicate that one or more of these new terms will be significant in many cases of gas flow in porous media.

Keywords: Advection; Diffusion; Slip flow; Volume averaging; Micro-scale coupling

1. Introduction

Knowledge of the underlying physics governing gas-phase transport in porous media is of considerable interest for many applications ranging from contaminant transport in soils to diffusion in porous catalysts. Recent laboratory studies [1] including those presented in Part 2 [2] have demonstrated that the traditional forms of the gas-phase, mass and momentum transport equations for porous media may not accurately describe the underlying physical phenomena. The flow scenarios examined in these studies were analogous to those expected in situations of environmental concern with all chemical and physical parameters measured independently. Numerical models based on traditional representations of the transport equations accurately matched the experimental data only for purely diffusive flow regimes (i.e. mass fractions less than 1×10^{-4} and no external driving forces). Outside of this flow regime model output did not match the data. In Part 1 of this work we utilize the method of volume averaging to derive macro-scale gas transport equations that are coupled at the closure level. In Part 2 we examine these newly derived equations through the use of laboratory experiments and numerical modeling.

The method of volume averaging provides a powerful tool with which to derive up-scaled conservation equations. This technique has been utilized in the derivation of Darcy's Law [3,4], multi-phase advection–dispersion equations [5–7] and heat transfer equations [8]. One of the principal advantages of using the method of volume averaging is that it provides a mathematical framework with which to directly derive volume averaged (porous media) conservation equations from well known and well understood point equations and boundary conditions. The development of closure problems which relate micro-scale and macro-scale parameters allows exact mathematical representations of up-scaled transport parameters. A full introduction to the method of volume averaging is provided by Whitaker [9].

The method of volume averaging can be represented schematically as in Fig. 1. Equations governing transport and transformation at the pore scale, such as

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Nomenclature

a_v interfacial area per unit volume, m^{-1}
$A_{\beta\sigma}$ area of the β–σ interface contained within the averaging volume, m^2
$A_{e\beta}$ area occupied by the β-phase at the outer surface of the averaging volume, m^2
D_{AB} binary molecular diffusion coefficient for species A and B, m^2/s
$\mathbf{D}_{eff}$ effective diffusion coefficient in porous media tensor, m^2/s
$\mathbf{g}$ gravitational acceleration vector, m/s^2
$\mathbf{I}$ unit tensor
$k = \frac{k}{k_{-1}}$ sorption/desorption rate constant in Langmuir type sorption relation, m
k_1 adsorption rate constant, m/s
k_{-1} desorption rate constant, s^{-1}
$\mathbf{k}_{sorb,\beta}$ sorptive "conductivity" vector in intrinsic velocity expression, m^4/kg
K^* adsorption rate constant, m^3/kg s
K sorption/desorption rate constant in Langmuir type sorption relation, m^3/kg
$\mathbf{K}_\beta$ permeability tensor, m^2
$\mathbf{K}_{slip,\beta}$ slip conductivity tensor, m^2/s
ℓ_β characteristic β-phase micro-length scale, m
L characteristic macro-length scale, m
M_A molecular weight of species A, g/mol
$\mathbf{n}_{\beta\sigma} = -\mathbf{n}_{\sigma\beta}$ unit normal vector directed from the β-phase to the σ-phase
p_β total β-phase pressure, Pa
$\langle p_\beta \rangle^\beta$ intrinsic average pressure in the β-phase, Pa
$\tilde{p}_\beta = p_\beta - \langle p_\beta \rangle^\beta$ local spatial deviation pressure, Pa
$\mathbf{r}$ position vector, m
$\mathbf{R}_\beta$ slip coupling tensor
R estimate of the magnitude of $\mathbf{R}_\beta$
$S(\langle \rho_{A\beta} \rangle^\beta)$ sorption coefficient, function of $\langle \rho_{A\beta} \rangle^\beta$
t time, s
t^* characteristic process time, s
$\mathbf{t}_{\beta\sigma}$ unit tangent vector between the β-phase and the σ-phase
$\mathbf{u}_A$ species A diffusive velocity vector, m/s
$\mathbf{v}_{A\beta} = \mathbf{u}_{A\beta} + \mathbf{v}_\beta$ species A total velocity vector, m/s
$\mathbf{v}_\beta$ mass average velocity vector in the β-phase, m/s
$\langle \mathbf{v}_\beta \rangle^\beta$ intrinsic average velocity vector in the β-phase, m/s
$\langle \mathbf{v}_\beta \rangle$ superficial average velocity vector in the β-phase, m/s
$\tilde{\mathbf{v}}_\beta = \mathbf{v}_\beta - \langle \mathbf{v}_\beta \rangle^\beta$ local spatial deviation velocity vector, m/s
V local averaging volume, m^3
$\mathbf{z}_{\beta\sigma} = \frac{D_{AB}\mathbf{t}_{\beta\sigma}}{\left(\frac{\langle \rho_{A\beta} \rangle^\beta}{\langle \rho_\beta \rangle^\beta}\right) + \alpha}$ slip coefficient utilized in the closure problem, m^2/s

Greek symbols
$\alpha = \frac{\sqrt{M_A}}{\sqrt{M_B} - \sqrt{M_A}}$ factor in the slip velocity expression
ε_β volume fraction of the β-phase
$\rho_{A\beta}$ species A mass density in the β-phase, kg/m^3
$\langle \rho_{A\beta} \rangle^\beta$ intrinsic average species A mass density, kg/m^3
$\tilde{\rho}_{A\beta} = \rho_{A\beta} - \langle \rho_{A\beta} \rangle^\beta$ local spatial deviation species A density, kg/m^3
ρ_{AS} total β-phase density, kg/m^2
ρ_β total β-phase density, kg/m^3
$\langle \rho_\beta \rangle^\beta$ intrinsic average total density, kg/m^3
$\tilde{\rho}_\beta = \rho_\beta - \langle \rho_\beta \rangle^\beta$ local spatial deviation total density, kg/m^3
μ_β β-phase viscosity, Pa s
$\omega_{A\beta}$ species A mass fraction
$\langle \omega_{A\beta} \rangle^\beta$ intrinsic average species A mass fraction
$\tilde{\omega}_{A\beta} = \omega_{A\beta} - \langle \omega_{A\beta} \rangle^\beta$ local spatial deviation species A mass fraction

Sub/superscripts
s solid surface
β gas phase
σ solid phase

Eqs. (6) and (7), are mathematically averaged, and macro-scale equations applicable at laboratory or field scales are obtained.

Two integral expressions are utilized to express averaged quantities,

$$\text{Superficial average:} \quad \langle F_\beta \rangle = \frac{1}{V} \int_{V_\beta(t)} F_\beta \, dV \tag{1a}$$

$$\text{Intrinsic average:} \quad \langle F_\beta \rangle^\beta = \frac{1}{V_\beta(t)} \int_{V_\beta(t)} F_\beta \, dV \tag{1b}$$

where "F_β" is an arbitrary β-phase scalar or tensor variable. The superficial and intrinsic averages are related by

$$\langle F_\beta \rangle = \varepsilon_\beta \langle F_\beta \rangle^\beta \tag{2}$$

where ε_β is the β-phase volume fraction, or porosity.

It is often convenient to represent point, or pore scale parameters as the sum of the intrinsic average and the deviation from the average:

$$F_\beta = \langle F_\beta \rangle^\beta + \tilde{F}_\beta \tag{3}$$

As one proceeds through the averaging process, expressions will often appear containing averaged and deviation quantities. The overall goal of the volume averaging process is to derive equations which contain only averaged quantities. This requires setting up "clo-

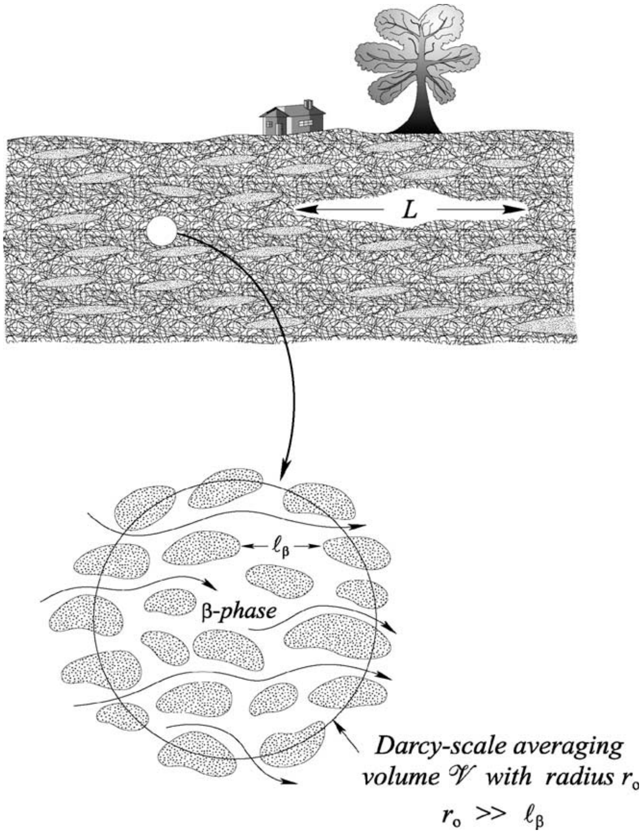

Fig. 1. Schematic representation of the volume averaging technique. ℓ_β is a representative pore length scale, r_0 is the radius of the averaging volume and L is a representative macro-scale length.

sure problems" which provide mathematical relationships between averaged and deviation quantities, in the form of boundary value problems. These boundary value problems provide the framework for precisely describing parameters such as the conductivity and dispersion coefficients which appear in the macro-scale equations.

Most of the volume averaging work to this point has focused on equations which are assumed to only be strongly coupled at the macro-scale. Coupling of equations at the closure level can be extremely complicated but may lead to new forms of the equations of interest. Many past studies have neglected closure level effects due simply to the fact that closure problems are often not developed. For coupling to occur, we would require both that the velocity affect the convective–diffusion equation *and* that the density affect the momentum equation. The first study of coupling at the closure level was conducted by Moyne et al. [10]. Following Moyne et al. [10], Whitaker [8] examined the process of coupled two-phase heat and mass transfer and found that closure-level coupling led to novel terms which did not appear in the non-coupled case. These two studies represent the totality of published work on closure level coupling as defined above.

Generally, gas-phase transport is described by the macro-scale coupling of volume averaged mass conservation equations with corresponding averaged momentum conservation equations. Subsurface environmental gas transport, for example, is often described by a mass transport equation

$$\left(\varepsilon_\beta + \underbrace{S(\langle\rho_{A\beta}\rangle^\beta)}_{\text{Adsorption coefficient}}\right)\frac{\partial\langle\rho_{A\beta}\rangle^\beta}{\partial t} = \underbrace{-\nabla\cdot\left(\langle\mathbf{v}_\beta\rangle\langle\rho_{A\beta}\rangle^\beta\right)}_{\text{Advection}} + \underbrace{\nabla\cdot\left[\rho_\beta\mathbf{D}\cdot\nabla\langle\omega_{A\beta}\rangle^\beta\right]}_{\text{Diffusion and dispersion}} \tag{4}$$

and Darcy's Law

$$\langle\mathbf{v}_\beta\rangle = -\frac{\mathbf{K}_\beta}{\mu_\beta}\cdot\left[\nabla\langle p_\beta\rangle^\beta - \rho_\beta\mathbf{g}\right] \tag{5}$$

where $\langle\mathbf{v}_\beta\rangle$ is the superficial average velocity, equivalent to the Darcy velocity often denoted by $\mathbf{q}_\beta$. We have used $\langle p_\beta\rangle^\beta$ to represent the *intrinsic* average pressure and $S(\langle\rho_{A\beta}\rangle^\beta)$ to represent an adsorption coefficient which may be a function of $\langle\rho_{A\beta}\rangle^\beta$. Each of these equations can be independently derived from point expressions for mass and momentum conservation (i.e. [9, Chapters 3 and 4]). When Eqs. (4) and (5) are utilized to describe flow in porous media, the coupling between the mass and momentum occurs both at the microscopic level, represented by mechanical dispersion, and at the macro-scale through the advective flux term in Eq. (4). Coupling at the closure level, which determines the behavior of the transport coefficients and the form of the driving forces, is not considered.

The gas-phase transport described by Eqs. (4) and (5) may be complicated by several additional factors due to the particular flow regimes of interest. The Dusty Gas Model is one equation set which attempts to account for several of these "non-ideal" transport phenomena. The Dusty Gas Model is based on dilute solution kinetic theory in which a single molecular species is assigned a zero velocity in order to represent the solid phase of a porous medium. The dusty gas equations are formulated to account for Knudsen diffusion (diffusion due to molecule–wall interactions when the pore size approaches the mean free path of the gaseous molecules), multi-component/non-dilute solution diffusive fluxes (utilizing a Stefan–Maxwell representation for the diffusive fluxes) and "diffusive" slip flow (an advective flux due to the existence of a finite, non-zero velocity at the pore walls, which exists for species of differing molecular masses). (for examples see [11–13]). The Dusty Gas Model is often presented as a more complete phenomenological approach than the traditional advection–dispersion mass transport equation coupled with an expression for the advective velocity. Due to the nature of the equation development, however, there is no theoretical means of determining the effective transport coefficients that appear in the model. The transport coefficients in the Dusty Gas Model must always be determined experimentally.

Other attempts at equation derivation include thermodynamic up-scaling work of the type popularized by Hassanizadeh and co-workers [14–17]. This approach entails up-scaling thermodynamic relationships, generally from the micro-scale to the macro-scale. In several papers [15,17], the authors examined the up-scaling of mass and momentum conservation expressions to arrive at equations analogous to Eqs. (4) and (5). The resultant macro-scale mass and momentum expressions contain novel terms which do not arise in the traditional development. As with the Dusty Gas Model, no closure problems are developed and values of the transport coefficients can only be obtained experimentally.

Up to this point, there has been no closure level, coupled up-scaling of the gas-phase mass and momentum equations. Although derivations of averaged mass and momentum equations are fairly common in the literature there are none which have attempted to couple the conservation equations at the closure level. As stated above, this type of coupling requires that the velocity affect the mass conservation equation and the species density affect the momentum equation *at the closure level*. The nature of the coupling can be seen by examination of the point equations represented as

Mass:

$$\text{Species:}\quad \frac{\partial \rho_{A\beta}}{\partial t} + \nabla \cdot (\rho_{A\beta}\mathbf{v}_{A\beta}) = 0 \tag{6a}$$

$$\text{B.C.1}\quad \mathbf{n}_{\beta\sigma} \cdot (\rho_{A\beta}\mathbf{v}_{A\beta}) = \frac{\partial \rho_{AS}}{\partial t} \quad \text{at } A_{\beta\sigma} \tag{6b}$$

$$\text{B.C.2}\quad \rho_{A\beta} = f(\mathbf{r}, t) \quad \text{at } A_{\beta e} \tag{6c}$$

$$\text{I.C.}\quad \rho_{A\beta} = g(\mathbf{r}) \quad \text{at } t = 0 \tag{6d}$$

$$\text{Total:}\quad \nabla \cdot \mathbf{v}_{\beta} = 0 \quad \text{in the } \beta\text{-phase} \tag{6e}$$

Total momentum:

$$0 = -\nabla p_{\beta} + \rho_{\beta}\mathbf{g} + \mu_{\beta}\nabla^2\mathbf{v}_{\beta} \quad \text{in the } \beta\text{-phase} \tag{7a}$$

$$\text{B.C.1}\quad \mathbf{v}_{\beta} \cdot \mathbf{t}_{\beta\sigma} = v_{\text{slip}} = \frac{D_{AB}\mathbf{t}_{\beta\sigma} \cdot \nabla\omega_{A\beta}}{\omega_{A\beta} + \alpha} \quad \text{at } A_{\beta\sigma} \tag{7b}$$

$$\text{B.C.2}\quad \mathbf{v}_{\beta} \cdot \mathbf{n}_{\beta\sigma} = 0 \quad \text{at } A_{\beta\sigma} \tag{7c}$$

$$\text{B.C.3}\quad \mathbf{v}_{\beta} = \mathbf{f}(\mathbf{r}, t) \quad \text{at } A_{\beta e} \tag{7d}$$

Coupling between mass and momentum transport occurs through Eq. (6a) and in the boundary conditions given by Eq. (6b) and (7b). The assumptions that lead to Eqs. (6e) and (7a)–(7d) are discussed in Appendix A. Here we have presented the species and total mass conservation equations and the total momentum equation. The species momentum conservation will be expressed by utilizing Fick's Law, as discussed below.

The first boundary condition (Eq. (7b)) in the momentum equation represents the tangential slip boundary condition at the pore walls. This condition states that the gas velocity will be finite and non-zero, tangential to the interface between the gas and solid phases. This phenomena was first noted experimentally by Graham [18] and provides the advective velocity necessitated by Graham's Law. The theory for binary flow in a capillary tube was first explored by Kramers and Kistemaker [19]. This theory (for a binary system) can be derived directly from kinetic theory, as demonstrated on a molar basis by Jackson [11]. It is easy to show that this condition will be important in flow regimes where neither diffusion nor advection is dominant. These are the types of flows that can be expected in many situations of environmental concern. In the case of advection dominated transport, this slip velocity tangential to the solid surface will become negligible relative to the mean velocity. It should be noted that this phenomenon is different than Knudsen slip mentioned above.

The purpose of this work is to utilize the method of volume averaging to simultaneously up-scale the point mass and momentum conservation equations represented by Eqs. (6) and (7), allowing for coupling at the closure level. In doing so, we hope to account for all important transport processes at the Darcy scale which arise due to coupling between the equations. We will consider the case of two species gas-phase flow in a dry porous medium. Mathematical constraints on the averaging procedure are developed and presented throughout the work. By utilizing derived closure expressions, we will obtain estimates for new macro-scale parameters.

2. Volume averaging

2.1. Mass conservation equations

The first step in the averaging process will be to examine the first boundary condition in the mass conservation problem. We will employ Fick's law, represented as $\mathbf{u}_{A\beta}\rho_{A\beta} = -\rho D_{AB}\nabla\omega_{A\beta}$ as our species momentum equation. This form of the equation can be derived directly from the Stefan–Maxwell equations and will only hold for binary or dilute solution systems. Utilizing the Langmuir–Hinshelwood formulation for sorptive interactions at the gas solid interface, and following the arguments presented in Appendix A.3, the first boundary condition in the mass conservation statement can be represented as

$$\text{B.C.1} \quad -\mathbf{n}_{\beta\sigma}\cdot\rho_\beta D_{AB}\nabla\omega_{A\beta} = \frac{(1-\omega_{A\beta})k}{(1+K\rho_{A\beta})^2}\frac{\partial\rho_{A\beta}}{\partial t} \quad \text{at } A_{\beta\sigma} \tag{8}$$

The form of this equation arises from the assumptions that have been made about the sorptive interactions at the β–σ interface. It is important to note that we have not assumed that $\mathbf{n}_{\beta\sigma}\cdot\mathbf{v}_\beta$ will be equal to zero in the mass conservation equations. As demonstrated in Appendix A, we may neglect terms containing $\mathbf{n}_{\beta\sigma}\cdot\mathbf{v}_\beta$ in the momentum equations, but in order to neglect this term in the mass conservation boundary condition, the fairly stringent "dilute solution" criteria of $O(\omega_{A\beta}) \ll 1$ must be met. In order to preserve the generality of this work we will not invoke the dilute solution restriction.

The mass fraction term in Eq. (8) can be expanded as

$$(1-\omega_{A\beta}) = \left(1-\langle\omega_{A\beta}\rangle^\beta - \tilde{\omega}_{A\beta}\right) \tag{9}$$

For traditional heat and mass transfer processes [5,9,20], the spatial deviation is related to the average by

$$\tilde{\omega}_{A\beta} = O\left(\langle\omega_{A\beta}\rangle^\beta \frac{\ell_\beta}{L}\right) \tag{10}$$

This indicates that we may estimate the order of magnitude of the deviation species density as the intrinsic average species density multiplied by the ratio of the micro- to macro-length scales. We can neglect the deviation mass fraction on the right-hand side of Eq. (9) with respect to average mass fraction subject to

$$\text{Constraint:} \quad \ell_\beta \ll L \tag{11}$$

The boundary condition given by Eq. (8) will thus take the form

$$\text{B.C.1} \quad -\mathbf{n}_{\beta\sigma}\cdot\rho_\beta D_{AB}\nabla\omega_{A\beta} = \frac{k\left(1-\langle\omega_{A\beta}\rangle^\beta\right)}{(1+K\rho_{A\beta})^2}\frac{\partial\rho_{A\beta}}{\partial t} \quad \text{at } A_{\beta\sigma} \tag{12}$$

The sorptive term, $k/(1+K\rho_{A\beta})^2$, can be expanded by utilizing the decomposition $\rho_{A\beta} = \langle\rho_{A\beta}\rangle^\beta + \tilde{\rho}_{A\beta}$ followed by a Taylor series expansion around $\tilde{\rho}_{A\beta} = 0$. Subject to plausible constraints, we will arrive at the relationship (for details see Appendix B.1.1)

$$\frac{k}{(1+K\rho_{A\beta})^2} = \frac{k}{\left(1+K\langle\rho_{A\beta}\rangle^\beta\right)^2} \tag{13}$$

Utilizing Eq. (13) in Eq. (12) yields

$$\text{B.C.1} \quad -\mathbf{n}_{\beta\sigma}\cdot\rho_\beta D_{AB}\nabla\omega_{A\beta} = \frac{k\left(1-\langle\omega_{A\beta}\rangle^\beta\right)}{\left(1+K\langle\rho_{A\beta}\rangle^\beta\right)^2}\frac{\partial\rho_{A\beta}}{\partial t} \quad \text{at } A_{\beta\sigma} \tag{14}$$

We will now turn our attention to developing the volume averaged form of the transport equation (Eq. (6a)). Employing a Fick's Law representation for binary diffusive flux allows us to express Eq. (6a) as

$$\frac{\partial\rho_{A\beta}}{\partial t} + \nabla\cdot(\rho_{A\beta}\mathbf{v}_\beta) = \nabla\cdot(\rho_\beta D_{AB}\nabla\omega_{A\beta}) \tag{15}$$

Following the arguments presented in Whitaker [9, Chapter 3] we can form the superficial average of Eq. (15), where we have employed the relationship represented by Eq. (2), and arrive at

$$\varepsilon_\beta\frac{\partial\langle\rho_{A\beta}\rangle^\beta}{\partial t} + \nabla\cdot(\varepsilon_\beta\langle\rho_{A\beta}\rangle^\beta\langle\mathbf{v}_\beta\rangle^\beta) + \nabla\cdot\langle\tilde{\rho}_{A\beta}\tilde{\mathbf{v}}_\beta\rangle + \frac{1}{V}\int_{A_{\beta\sigma}}\mathbf{n}_{\beta\sigma}\cdot\rho_{A\beta}\mathbf{v}_\beta\,dA = \langle\nabla\cdot(\rho_\beta D_{AB}\nabla\omega_{A\beta})\rangle \tag{16}$$

The area integral term arises from the fact that the component of the advective velocity normal to the β–σ interface cannot be neglected in the mass conservation problem as stated above. The term on the right-hand side of Eq. (16) can be expanded by utilizing the spatial averaging theorem [9, Section 1.2.1] to yield

$$\varepsilon_\beta\frac{\partial\langle\rho_{A\beta}\rangle^\beta}{\partial t} + \nabla\cdot\left(\varepsilon_\beta\langle\rho_{A\beta}\rangle^\beta\langle\mathbf{v}_\beta\rangle^\beta\right) + \nabla\cdot\langle\tilde{\rho}_{A\beta}\tilde{\mathbf{v}}_\beta\rangle + \frac{1}{V}\int_{A_{\beta\sigma}}\mathbf{n}_{\beta\sigma}\cdot\left(\rho_{A\beta}\mathbf{v}_\beta - \rho_\beta D_{AB}\nabla\omega_{A\beta}\right)dA = \nabla\cdot\langle\rho_\beta D_{AB}\nabla\omega_{A\beta}\rangle \tag{17}$$

Utilizing B.C.1 as represented by Eq. (A.28) and the relationship given by Eq. (13) this becomes

$$\varepsilon_\beta\frac{\partial\langle\rho_{A\beta}\rangle^\beta}{\partial t} + \nabla\cdot\left(\varepsilon_\beta\langle\rho_{A\beta}\rangle^\beta\langle\mathbf{v}_\beta\rangle^\beta\right) + \nabla\cdot\langle\tilde{\rho}_{A\beta}\tilde{\mathbf{v}}_\beta\rangle + \frac{k}{\left(1+K\langle\rho_{A\beta}\rangle^\beta\right)^2}\frac{1}{V}\int_{A_{\beta\sigma}}\frac{\partial\rho_{A\beta}}{\partial t}\,dA = \nabla\cdot\langle\rho_\beta D_{AB}\nabla\omega_{A\beta}\rangle \tag{18}$$

We will now proceed with further simplifications to the area integral term in Eq. (18). Following the example presented by Ochoa-Tapia et al. [21] we can exchange differentiation and integration. The area averaged species density can be further simplified as indicated in Whitaker [9, Section 1.3.3]. This simplification entails expressing the area averaged species density in terms of the volume averaged species density by means of a Taylor series expansion around the centroid of the averaging volume. Higher order terms are eliminated and we arrive at the estimate that the area averaged species density can be approximated by the volume averaged species density. We will be able to express Eq. (18) as

$$\varepsilon_\beta \frac{\partial \langle \rho_{A\beta}\rangle^\beta}{\partial t} + \nabla \cdot (\varepsilon_\beta \langle \rho_{A\beta}\rangle^\beta \langle \mathbf{v}_\beta\rangle^\beta) + \nabla \cdot \langle \tilde{\rho}_{A\beta} \tilde{\mathbf{v}}_\beta \rangle + a_v \frac{k}{(1+K\langle \rho_{A\beta}\rangle^\beta)^2} \frac{\partial \langle \rho_{A\beta}\rangle^\beta}{\partial t} = \nabla \cdot \langle \rho_\beta D_{AB} \nabla \omega_{A\beta}\rangle \tag{19}$$

subject to the constraint that the radius of the averaging volume is significantly less than a representative macroscopic length scale.

We now focus our attention on the term on the right hand side of Eq. (19). We assume that variations of both D_{AB} and ρ_β can be neglected within the averaging volume. This allows us to simplify the diffusive term according to

$$\langle \rho_\beta D_{AB} \nabla \omega_{A\beta}\rangle = \rho_\beta D_{AB} \langle \nabla \omega_{A\beta}\rangle \tag{20}$$

This simplification for the total density, ρ_β, is based on Eqs. (9)–(11) as they apply to $\langle \rho_\beta\rangle^\beta$ and $\tilde{\rho}_\beta$. At this point, we make use of the spatial averaging theorem a second time and follow the development given by Whitaker [9, Section 1.3] in order to expand the diffusive term and express Eq. (19) in the form

$$\begin{aligned}\varepsilon_\beta \frac{\partial \langle \rho_{A\beta}\rangle^\beta}{\partial t} = & -\nabla \cdot \left(\varepsilon_\beta \langle \rho_{A\beta}\rangle^\beta \langle \mathbf{v}_\beta\rangle^\beta\right) - \nabla \cdot \langle \tilde{\rho}_{A\beta} \tilde{\mathbf{v}}_\beta\rangle \\ & + \nabla \cdot \left(D_{AB}\rho_\beta \varepsilon_\beta \nabla \langle \omega_{A\beta}\rangle^\beta\right) \\ & + \nabla \cdot \left(D_{AB}\rho_\beta \frac{1}{V}\int_{A_{\beta\sigma}} \mathbf{n}_{\beta\sigma} \tilde{\omega}_{A\beta}\, dA\right) \\ & - a_v \frac{k}{\left(1+K\langle \rho_{A\beta}\rangle^\beta\right)^2} \frac{\partial \langle \rho_{A\beta}\rangle^\beta}{\partial t}\end{aligned} \tag{21}$$

If we assume $\nabla \varepsilon_\beta = 0$ and divide Eq. (21) by ε_β, we arrive at the unclosed form of the averaged species continuity equation

$$\begin{aligned}\frac{\partial \langle \rho_{A\beta}\rangle^\beta}{\partial t} = & -\nabla \cdot \left(\langle \mathbf{v}_\beta\rangle^\beta \langle \rho_{A\beta}\rangle^\beta\right) - \varepsilon_\beta^{-1} \nabla \cdot \langle \tilde{\rho}_{A\beta} \tilde{\mathbf{v}}_\beta\rangle \\ & + \varepsilon_\beta^{-1} \nabla \cdot \left(D_{AB}\rho_\beta \varepsilon_\beta \nabla \langle \omega_{A\beta}\rangle^\beta\right) \\ & + \varepsilon_\beta^{-1} \nabla \cdot \left(D_{AB}\rho_\beta \frac{1}{V}\int_{A_{\beta\sigma}} \mathbf{n}_{\beta\sigma} \tilde{\omega}_{A\beta}\, dA\right) \\ & - a_v \varepsilon_\beta^{-1} \frac{k}{\left(1+K\langle \rho_{A\beta}\rangle^\beta\right)^2} \frac{\partial \langle \rho_{A\beta}\rangle^\beta}{\partial t}\end{aligned} \tag{22a}$$

along with the boundary conditions given by

$$\text{B.C.1} \quad -\mathbf{n}_{\beta\sigma} \nabla \cdot \rho_\beta D_{AB} \nabla \omega_{A\beta} = \frac{k\left(1-\langle \omega_{A\beta}\rangle^\beta\right)}{\left(1+K\langle \rho_{A\beta}\rangle^\beta\right)^2} \frac{\partial \rho_{A\beta}}{\partial t} \quad \text{at } A_{\beta\sigma} \tag{22b}$$

$$\text{B.C.2} \quad \tilde{\rho}_{A\beta} = f(\mathbf{r}, t) \quad \text{at } A_{\beta e} \tag{22c}$$

$$\text{I.C.} \quad \tilde{\rho}_{A\beta} = g(\mathbf{r}), \quad t = 0 \tag{22d}$$

In order to develop a closed form of Eq. (22a), we will need to develop a closure problem from which we can derive expressions for the deviation quantities which appear in Eq. (22a). In brief, a complete statement of the closure equations requires the development of boundary value problems for each of the deviation quantities of interest. The process begins by subtracting the unclosed averaged equation (Eq. (22a)) from the point equation (Eq. (15)), utilizing the representation for point quantities given by Eq. (7) yielding a partial differential equation for the deviation of the species density. This equation can then be simplified by employing reasonable constraints. Following the detailed derivation given in Appendix B.1.2, we will arrive at a boundary value problem for the species density deviation (referred to as a closure problem) which can be expressed as

$$\underbrace{\nabla \cdot (\tilde{\mathbf{v}}_\beta \langle \rho_{A\beta}\rangle^\beta)}_{\text{Coupling and source}} + \nabla \cdot (\mathbf{v}_\beta \tilde{\rho}_{A\beta}) = \nabla \cdot D_{AB} \nabla \tilde{\rho}_{A\beta} + \underbrace{a_v \varepsilon_\beta^{-1} \frac{k}{\left(1+K\langle \rho_{A\beta}\rangle^\beta\right)^2} \frac{\partial \langle \rho_{A\beta}\rangle^\beta}{\partial t}}_{\text{Source}} \tag{23a}$$

$$\begin{aligned}\text{B.C.1} \quad -\mathbf{n}_{\beta\sigma} D_{AB} \cdot \nabla \tilde{\rho}_{A\beta} = & \underbrace{\mathbf{n}_{\beta\sigma} \cdot D_{AB} \langle \rho_\beta\rangle^\beta \nabla \left(\frac{\langle \rho_{A\beta}\rangle^\beta}{\langle \rho_\beta\rangle^\beta}\right)}_{\text{Source}} \\ & + \underbrace{\frac{k\left(1-\left(\frac{\langle \rho_{A\beta}\rangle^\beta}{\langle \rho_\beta\rangle^\beta}\right)\right)}{(1+K\langle \rho_{A\beta}\rangle^\beta)^2} \frac{\partial \langle \rho_{A\beta}\rangle^\beta}{\partial t}}_{\text{Source}} \quad \text{at } A_{\beta\sigma}\end{aligned} \tag{23b}$$

$$\text{Periodicity:} \quad \tilde{\rho}_{A\beta}(\mathbf{r}+\ell_i) = \tilde{\rho}_{A\beta}(\mathbf{r}), \quad i = 1,2,3 \tag{23c}$$

where all terms containing averaged species densities are identified as sources for the deviation species density.

2.2. Momentum conservation equations

The boundary value problem for momentum conservation is presented by Eqs. (7). It is important to note that, based on the arguments presented in Appendix A, boundary condition represented by Eq. (7c) will be valid for the point momentum conservation equations although it *will not be valid for the point mass conservation equations* (see Eqs. (A.29)–(A.33)).

Following the methods of Whitaker [9, Chapter 4] we may form the volume average of Eq. (7a) and obtain

$$0 = -\varepsilon_\beta \nabla \langle p_\beta \rangle^\beta - \frac{1}{V}\int_{A_{\beta\sigma}} \mathbf{n}_{\beta\sigma}\tilde{p}_\beta \, \mathrm{d}A + \varepsilon_\beta \rho_\beta \mathbf{g} + \mu_\beta \left[\nabla \cdot \langle \nabla \mathbf{v}_\beta \rangle + \frac{1}{V}\int_{A_{\beta\sigma}} \mathbf{n}_{\beta\sigma} \cdot \nabla \mathbf{v}_\beta \, \mathrm{d}A \right] \tag{24}$$

It must be noted that several constraints underlie Eq. (24). We have assumed that variations in the viscosity and total density can be neglected within the averaging volume. Restrictions have been invoked to constrain variations in the porosity. The representative micro-scale is constrained to be significantly smaller than the radius of the averaging volume, and the radius of the averaging volume must be significantly smaller than a representative macro-scale.

The bracketed term in Eq. (24) can be further expanded by applying the spatial averaging theorem. Remembering that at the β–σ interface $\mathbf{v}_\beta = \mathbf{t}_{\beta\sigma} v_{\mathrm{slip}}$, and following Whitaker [9, Section 4.1.2], the bracketed term can be expanded as

$$\begin{aligned} \nabla \cdot \langle \nabla \mathbf{v}_\beta \rangle + \frac{1}{V}\int_{A_{\beta\sigma}} \mathbf{n}_{\beta\sigma} \cdot \nabla \mathbf{v}_\beta \, \mathrm{d}A &= \nabla^2 \left(\varepsilon_\beta \langle \mathbf{v}_\beta \rangle^\beta \right) + \nabla \cdot \left[\frac{1}{V}\int_{A_{\beta\sigma}} \mathbf{n}_{\beta\sigma} \mathbf{t}_{\beta\sigma} v_{\mathrm{slip}} \, \mathrm{d}A \right] \\ &\quad - \nabla \varepsilon_\beta \cdot \nabla \langle \mathbf{v}_\beta \rangle^\beta + \frac{1}{V}\int_{A_{\beta\sigma}} \mathbf{n}_{\beta\sigma} \cdot \nabla \tilde{\mathbf{v}}_\beta \, \mathrm{d}A \end{aligned} \tag{25}$$

Order of magnitude estimates of the two integral terms on the right-hand side of Eq. (25) can be expressed as

$$\nabla \cdot \left[\frac{1}{V}\int_{A_{\beta\sigma}} \mathbf{n}_{\beta\sigma} \mathbf{t}_{\beta\sigma} v_{\mathrm{slip}} \, \mathrm{d}A \right] = \mathrm{O}\left(\frac{a_{\mathrm{v}} \langle \mathbf{v}_\beta \rangle^\beta}{L} \right) \tag{26a}$$

and

$$\frac{1}{V}\int_{A_{\beta\sigma}} \mathbf{n}_{\beta\sigma} \cdot \nabla \tilde{\mathbf{v}}_\beta \, \mathrm{d}A = \mathrm{O}\left(\frac{a_{\mathrm{v}} \langle \mathbf{v}_\beta \rangle^\beta}{\ell_\beta} \right) \tag{26b}$$

The appropriate length scale in Eq. (26a) is the macro-scale because it is associated with the divergence of an area averaged slip velocity, while in Eq. (26b) we utilize the micro-length scale because we have the divergence of a deviation velocity. In Eq. (26a) we have assumed that the slip velocity will be the same order of magnitude as $\langle \mathbf{v}_\beta \rangle^\beta$. On the basis of these estimates we may neglect the first integral term on the left-hand side with respect to the second term constrained by $\ell_\beta \ll L$. Eq. (24) can thus be expressed as

$$0 = -\varepsilon_\beta \nabla \langle p_\beta \rangle^\beta + \varepsilon_\beta \rho_\beta \mathbf{g} + \mu_\beta \nabla^2 \left(\varepsilon_\beta \langle \mathbf{v}_\beta \rangle^\beta \right) - \mu_\beta \nabla \varepsilon_\beta \cdot \nabla \langle \mathbf{v}_\beta \rangle^\beta + \frac{1}{V}\int_{A_{\beta\sigma}} \mathbf{n}_{\beta\sigma} \cdot [-\mathbf{I}\tilde{p}_\beta + \mu_\beta \nabla \tilde{\mathbf{v}}_\beta] \, \mathrm{d}A \tag{27}$$

If we neglect all terms containing $\nabla \varepsilon_\beta$ and divide by ε_β we will obtain the unclosed form of the volume averaged momentum equation containing both average and deviation quantities

$$0 = -\nabla \langle p_\beta \rangle^\beta + \rho_\beta \mathbf{g} + \mu_\beta \nabla^2 \langle \mathbf{v}_\beta \rangle^\beta + \varepsilon_\beta^{-1} \frac{1}{V}\int_{A_{\beta\sigma}} \mathbf{n}_{\beta\sigma} \cdot [-\mathbf{I}\tilde{p}_\beta + \mu_\beta \nabla \tilde{\mathbf{v}}_\beta] \, \mathrm{d}A \tag{28}$$

As in the mass averaging process, we subtract this volume averaged equation from the point equation (Eq. (7a)). The spatial deviation momentum equation can be expressed as

$$0 = -\nabla \tilde{p}_\beta + \mu_\beta \nabla^2 \tilde{\mathbf{v}}_\beta - \varepsilon_\beta^{-1} \frac{1}{V}\int_{A_{\beta\sigma}} \mathbf{n}_{\beta\sigma} \cdot [-\mathbf{I}\tilde{p}_\beta + \mu_\beta \nabla \tilde{\mathbf{v}}_\beta] \, \mathrm{d}A \tag{29}$$

Examining the first boundary condition (Eq. (7b)), we expand $\mathbf{v}_\beta$ and $\omega_{\mathrm{A}\beta}$ into their average and deviation. We then utilize Eqs. (10) and (11) in order to obtain the relationship $\langle \omega_{\mathrm{A}\beta} \rangle^\beta \gg \tilde{\omega}_{\mathrm{A}\beta}$, allowing us to express the boundary condition as

$$\text{B.C.1} \quad \tilde{\mathbf{v}}_\beta \cdot \mathbf{t}_{\beta\sigma} = \frac{D_{\mathrm{AB}} \mathbf{t}_{\beta\sigma} \cdot \nabla \langle \omega_{\mathrm{A}\beta} \rangle^\beta}{\langle \omega_{\mathrm{A}\beta} \rangle^\beta + \alpha} + \frac{D_{\mathrm{AB}} \mathbf{t}_{\beta\sigma} \cdot \nabla \tilde{\omega}_{\mathrm{A}\beta}}{\langle \omega_{\mathrm{A}\beta} \rangle^\beta + \alpha} - \langle \mathbf{v}_\beta \rangle^\beta \cdot \mathbf{t}_{\beta\sigma} \quad \text{at } A_{\beta\sigma} \tag{30}$$

where it should be noted that we cannot a priori eliminate $\nabla \tilde{\omega}_{\mathrm{A}\beta}$ with respect $\nabla \langle \omega_{\mathrm{A}\beta} \rangle^\beta$ because of the difference in length scales associated with $\langle \omega_{\mathrm{A}\beta} \rangle^\beta$ and $\tilde{\omega}_{\mathrm{A}\beta}$. As in the mass closure problem (Eqs. (23), governing the deviation species density), we would like to express the average and deviation of the mass fraction in terms of the averaged total density and the average and deviation of the species densities, respectively (see Eqs. (B.32)–(B.34))). Based on these representations we can state the full simplified momentum closure problem (governing the deviation velocity and pressure) as

$$0 = -\nabla \tilde{p}_\beta + \mu_\beta \nabla^2 \tilde{\mathbf{v}}_\beta - \varepsilon^{-1} \beta \frac{1}{V}\int_{A_{\beta\sigma}} \mathbf{n}_{\beta\sigma} \cdot [-\mathbf{I}\tilde{p}_\beta + \mu_\beta \nabla \tilde{\mathbf{v}}_\beta] \, \mathrm{d}A \tag{31a}$$

$$\nabla \cdot \tilde{\mathbf{v}}_\beta = 0 \tag{31b}$$

$$\text{B.C.1} \quad \tilde{\mathbf{v}}_\beta \cdot \mathbf{t}_{\beta\sigma} = \underbrace{\frac{D_{\mathrm{AB}} \mathbf{t}_{\beta\sigma} \cdot \nabla \left(\langle \rho_{\mathrm{A}\beta} \rangle^\beta / \langle \rho_\beta \rangle^\beta \right)}{\left(\langle \rho_{\mathrm{A}\beta} \rangle^\beta / \langle \rho_\beta \rangle^\beta \right) + \alpha}}_{\text{Source}} + \underbrace{\frac{D_{\mathrm{AB}} \mathbf{t}_{\beta\sigma} \cdot \nabla \left(\tilde{\rho}_{\mathrm{A}\beta} / \langle \rho_\beta \rangle^\beta \right)}{\left(\langle \rho_{\mathrm{A}\beta} \rangle^\beta / \langle \rho_\beta \rangle^\beta \right) + \alpha}}_{\text{Coupling}} - \underbrace{\langle \mathbf{v}_\beta \rangle^\beta \cdot \mathbf{t}_{\beta\sigma}}_{\text{Source}} \quad \text{at } A_{\beta\sigma} \tag{31c}$$

$$\text{B.C.2} \quad \tilde{\mathbf{v}}_\beta \cdot \mathbf{n}_{\beta\sigma} = \underbrace{-\langle \mathbf{v}_\beta \rangle^\beta \cdot \mathbf{n}_{\beta\sigma}}_{\text{Source}} \quad \text{at } A_{\beta\sigma} \tag{31d}$$

$$\text{Periodicity:} \quad \tilde{p}_\beta(\mathbf{r} + \ell_i) = \tilde{p}_\beta(\mathbf{r}), \quad \tilde{\mathbf{v}}_\beta(\mathbf{r} + \ell_i) = \tilde{\mathbf{v}}_\beta(\mathbf{r}), \quad i = 1,2,3 \tag{31e}$$

$$\text{Average:} \quad \langle \tilde{\mathbf{v}}_\beta \rangle^\beta = 0 \tag{31f}$$

The expression for the deviation continuity equation (Eq. (31b)) is obtained directly from arguments presented in Whitaker [9, Section 4.2.2] which demonstrate that the source which appears in this continuity equation will be negligible compared to the source in Eq. (31d). The arguments in favor of replacing the third boundary condition with the periodicity condition represented by Eq. (31e) are explained in Whitaker [9, Section 4.2.5].

3. Coupled closure

3.1. Closure variables and boundary value problems

In order to complete the closure process and solve for $\tilde{\rho}_{A\beta}$, $\tilde{v}_\beta$, and $\tilde{p}_\beta$, we will need to define closure variables which will account for the coupling between the averaged mass and momentum transport equations. The closure variables relate the sources identified in Eqs. (23) and (31) to $\tilde{\rho}_{A\beta}$, $\tilde{v}_\beta$, and $\tilde{p}_\beta$. By doing so we can obtain an understanding of how averaged parameters relate to and control the behavior of the deviation variables. The deviation velocity, pressure and species density can be represented by closure variables and volume averaged quantities in the following manner:

$$\tilde{\mathbf{v}}_\beta = \mathbf{B}_\beta \cdot \langle \mathbf{v}_\beta \rangle^\beta + \mathbf{C}_\beta \cdot \nabla\left(\frac{\langle \rho_{A\beta} \rangle^\beta}{\langle \rho_\beta \rangle^\beta}\right) + \mathbf{h}_\beta \frac{k}{(1 + K\langle \rho_{A\beta} \rangle^\beta)^2} \frac{\partial \langle \rho_{A\beta} \rangle^\beta}{\partial t} \tag{32}$$

$$\tilde{p}_\beta = \mu_\beta \mathbf{b}_\beta \cdot \langle \mathbf{v} \rangle^\beta + \mu_\beta \mathbf{c}_\beta \cdot \nabla\left(\frac{\langle \rho_{A\beta} \rangle^\beta}{\langle \rho_\beta \rangle^\beta}\right) + \mu_\beta j_\beta \frac{k}{(1 + K\langle \rho_{A\beta} \rangle^\beta)^2} \frac{\partial \langle \rho_{A\beta} \rangle^\beta}{\partial t} \tag{33}$$

$$\tilde{\rho}_{A\beta} = \mathbf{d}_\beta \cdot \langle \mathbf{v}_\beta \rangle^\beta + \mathbf{e}_\beta \cdot \nabla\left(\frac{\langle \rho_{A\beta} \rangle^\beta}{\langle \rho_\beta \rangle^\beta}\right) + f_\beta \frac{k}{(1 + K\langle \rho_{A\beta} \rangle^\beta)^2} \frac{\partial \langle \rho_{A\beta} \rangle^\beta}{\partial t} \tag{34}$$

Governing equations for the closure variables ($\mathbf{B}_\beta$, $\mathbf{C}_\beta$, $\mathbf{h}_\beta$, $\mathbf{b}_\beta$, $\mathbf{c}_\beta$, j_β, $\mathbf{d}_\beta$, $\mathbf{e}_\beta$, f_β) can be obtained by utilizing the method of superposition, following the techniques utilized in other volume averaging studies [3,5,6,9]. It must be noted that there is no proof of superposition when local thermal equilibrium is not valid. On the other hand, the comparison between theory and experiment [22, p. 441 and 446] suggests that superposition is an acceptable approximation for the very severe cases that were examined therein. Expressions for the closure variables are determined by the boundary value problems presented in Appendix C.

3.2. Closed momentum equation and simplifications

In order to fully close the volume averaged momentum equation, the expressions given by Eqs. (32)–(34) must be substituted into the unclosed averaged equation (Eq. (28)) yielding

$$\begin{aligned} 0 = {} & -\nabla\langle p_\beta \rangle^\beta + \rho_\beta \mathbf{g} + \mu_\beta \nabla^2 \langle \mathbf{v}_\beta \rangle^\beta \\ & + \left[\varepsilon_\beta^{-1} \frac{1}{V} \int_{A_{\beta\sigma}} \mathbf{n}_{\beta\sigma} \cdot [-\mu_\beta \mathbf{I} \mathbf{b}_\beta + \mu_\beta \nabla \mathbf{B}_\beta]\, \mathrm{d}A\right] \cdot \langle \mathbf{v}_\beta \rangle^\beta \\ & + \left[\varepsilon_\beta^{-1} \frac{1}{V} \int_{A_{\beta\sigma}} \mathbf{n}_{\beta\sigma} \cdot [-\mu_\beta \mathbf{I} \mathbf{c}_\beta + \mu_\beta \nabla \mathbf{C}_\beta]\, \mathrm{d}A\right] \cdot \nabla\langle \omega_{A\beta} \rangle^\beta \\ & + \left[\varepsilon_\beta^{-1} \frac{1}{V} \int_{A_{\beta\sigma}} \mathbf{n}_{\beta\sigma} \cdot [-\mu_\beta \mathbf{I} j_\beta + \mu_\beta \nabla \mathbf{h}_\beta] \times \frac{k}{\left(1 + K\langle \rho_{A\beta} \rangle^\beta\right)^2} \mathrm{d}A\right] \frac{\partial \langle \rho_{A\beta} \rangle^\beta}{\partial t} \end{aligned} \tag{35}$$

Utilizing the definitions

$$\left[\varepsilon_\beta^{-1} \frac{1}{V} \int_{A_{\beta\sigma}} \mathbf{n}_{\beta\sigma} \cdot [-\mathbf{I} \mathbf{b}_\beta + \nabla \mathbf{B}_\beta]\, \mathrm{d}A\right] = -\varepsilon_\beta \mathbf{K}_\beta^{-1} \tag{36}$$

$$\left[\varepsilon_\beta^{-1} \frac{1}{V} \int_{A_{\beta\sigma}} \mathbf{n}_{\beta\sigma} \cdot [-\mathbf{I} \mathbf{c}_\beta + \nabla \mathbf{C}_\beta]\, \mathrm{d}A\right] = \mathbf{L}_\beta \tag{37}$$

$$\frac{k}{\left(1 + K\langle \rho_{A\beta} \rangle^\beta\right)^2} \left[\varepsilon_\beta^{-1} \frac{1}{V} \int_{A_{\beta\sigma}} \mathbf{n}_{\beta\sigma} \cdot [-\mathbf{I} j_\beta + \nabla \mathbf{h}_\beta]\, \mathrm{d}A\right] = \mathbf{m}_\beta \tag{38}$$

and the relationship $\varepsilon_\beta \langle \mathbf{v}_\beta \rangle^\beta = \langle \mathbf{v}_\beta \rangle$ we will arrive at

$$\langle \mathbf{v}_\beta \rangle = -\frac{\mathbf{K}_\beta}{\mu_\beta} \cdot [\nabla\langle p_\beta \rangle^\beta - \rho_\beta \mathbf{g}] + \mathbf{K}_{\text{slip},\beta} \cdot \nabla\langle \omega_{A\beta} \rangle^\beta + \mathbf{K}_\beta \cdot \nabla^2 \langle \mathbf{v}_\beta \rangle^\beta + \mathbf{k}_{\text{sorb},\beta} \frac{\partial \langle \rho_{A\beta} \rangle^\beta}{\partial t} \tag{39}$$

where $\mathbf{K}_{slip,\beta} = \mathbf{L}_\beta \cdot \mathbf{K}_\beta$ is a macroscopic slip "conductivity" and $\mathbf{k}_{sorb,\beta} = \mathbf{m}_\beta \cdot \mathbf{K}_\beta$ is a sorptive "conductivity". The third term on the right-hand side is known as the Brinkman correction and will generally be negligible on the basis of the length scale constraints imposed in the derivation of Eq. (39) (see [9, Section 4.2.6]).

In order to be able to more readily utilize the fully closed momentum equation represented by Eq. (39) we need to obtain expressions for the two "conductivity" tensors $\mathbf{K}_\beta$, $\mathbf{K}_{slip,\beta}$ and the sorptive "conductivity" vector $\mathbf{k}_{sorb,\beta}$. The traditional permeability term has been explored elsewhere [9] and we will retain the form presented therein. Exact solutions for the other two "conductivity" terms could be obtained by solving the closure variable equations (Eqs. (C.3)–(C.8)). Due to the difficulty in obtaining solutions to these equations, we will focus on obtaining estimates for these two new terms in the velocity equation. Following the presentation contained in Appendix C and neglecting the Brinkman correction, we arrive at the form of the coupled momentum equation for gas flow in porous media based on order of magnitude estimates of the derived conductivity terms

$$\langle \mathbf{v}_\beta \rangle = -\frac{\mathbf{K}_\beta}{\mu_\beta} \cdot \left[\nabla \langle p_\beta \rangle^\beta - \rho_\beta \mathbf{g} \right] + \mathbf{K}_{slip,\beta} \cdot \nabla \langle \omega_{A\beta} \rangle^\beta + \mathbf{k}_{sorb,\beta} \frac{\partial \langle \rho_{A\beta} \rangle^\beta}{\partial t} \tag{40}$$

where our order of magnitude estimates indicate that

$$\mathbf{k}_{sorb,\beta} = \mathrm{O}\left[\left(\frac{k}{\left(1 + K\langle \rho_{A\beta} \rangle^\beta\right)} \right) \left(\frac{\langle \omega_{A\beta} \rangle^\beta - 1}{\langle \rho_{A\beta} \rangle^\beta + \langle \rho_\beta \rangle^\beta \alpha} \right) \right] \tag{41}$$

and

$$\mathbf{K}_{slip,\beta} = \mathrm{O}\left(\frac{D_{A\beta}}{\langle \omega_{A\beta} \rangle^\beta + \alpha} \right) \tag{42}$$

3.3. Closed mass conservation equation and simplifications

The closed form of the volume averaged mass conservation equation is obtained by first utilizing the relationship $\tilde{\omega} = \tilde{\rho}_{A\beta} / \langle \rho_\beta \rangle^\beta$ and the approximation $\rho_\beta = \langle \rho_\beta \rangle^\beta$ in the final term of Eq. (22a). We then substitute our expressions for the deviation density and velocity equations (32) and (34) into Eq. (22a) and arrive at

$$\begin{aligned}
&\left(1 + a_v \varepsilon_\beta^{-1} \frac{k}{(1 + K\langle \rho_{A\beta} \rangle^\beta)^2} \right) \frac{\partial \langle \rho_{A\beta} \rangle^\beta}{\partial t} \\
&= -\varepsilon_\beta^{-1} \nabla \cdot \left\langle \tilde{\mathbf{v}}_\beta \left(\mathbf{d}_\beta \cdot \langle \mathbf{v}_\beta \rangle^\beta + \mathbf{e}_\beta \cdot \nabla \langle \omega_{A\beta} \rangle^\beta + f_\beta \frac{k}{(1 + K\langle \rho_{A\beta} \rangle^\beta)^2} \frac{\partial \langle \rho_{A\beta} \rangle^\beta}{\partial t} \right) \right\rangle \\
&\quad + \varepsilon_\beta^{-1} \nabla \cdot \left[D_{AB} \frac{1}{V} \int_{A_{\beta\sigma}} \mathbf{n}_{\beta\sigma} \left(\mathbf{d}_\beta \cdot \langle \mathbf{v}_\beta \rangle^\beta + \mathbf{e}_\beta \cdot \nabla \langle \omega_{A\beta} \rangle^\beta + f_\beta \frac{k}{\left(1 + K\langle \rho_{A\beta} \rangle^\beta\right)^2} \frac{\partial \langle \rho_{A\beta} \rangle^\beta}{\partial t} \right) \mathrm{d}A \right] \\
&\quad - \nabla \cdot \left(\langle \mathbf{v}_\beta \rangle^\beta \langle \rho_{A\beta} \rangle^\beta \right) + \varepsilon_\beta^{-1} \nabla \cdot \left(D_{AB} \rho_\beta \varepsilon_\beta \nabla \langle \omega_{A\beta} \rangle^\beta \right)
\end{aligned} \tag{43}$$

Grouping the closure terms containing similar volume averaged variables allows us to express Eq. (43) as

$$\begin{aligned}
&\left(1 + a_v \varepsilon_\beta^{-1} \frac{k}{\left(1 + K\langle \rho_{A\beta} \rangle^\beta\right)^2} \right) \frac{\partial \langle \rho_{A\beta} \rangle^\beta}{\partial t} \\
&= -\nabla \cdot \left(\langle \mathbf{v}_\beta \rangle^\beta \langle \rho_{A\beta} \rangle^\beta \right) + \varepsilon_\beta^{-1} \nabla \cdot \left(D_{AB} \rho_\beta \varepsilon_\beta \nabla \langle \omega_{A\beta} \rangle^\beta \right) \\
&\quad + \varepsilon_\beta^{-1} \nabla \cdot \left[\frac{k}{\left(1 + K\langle \rho_{A\beta} \rangle^\beta\right)^2} \left\{ D_{AB} \left(\frac{1}{V} \int_{A_{\beta\sigma}} \mathbf{n}_{\beta\sigma} f_\beta \, \mathrm{d}A \right) - \langle \tilde{\mathbf{v}}_\beta f_\beta \rangle \right\} \frac{\partial \langle \rho_{A\beta} \rangle^\beta}{\partial t} \right] \\
&\quad + \varepsilon_\beta^{-1} \nabla \cdot \left[\left\{ D_{AB} \left(\frac{1}{V} \int_{A_{\beta\sigma}} \mathbf{n}_{\beta\sigma} \mathbf{d}_\beta \, \mathrm{d}A \right) - \langle \tilde{\mathbf{v}}_\beta \mathbf{d}_\beta \rangle \right\} \cdot \langle \mathbf{v}_\beta \rangle^\beta \right] \\
&\quad + \varepsilon_\beta^{-1} \nabla \cdot \left[\left\{ D_{AB} \rho_\beta \varepsilon_\beta \left(\rho_\beta^{-1} \frac{1}{V} \int_{A_{\beta\sigma}} \mathbf{n}_{\beta\sigma} \mathbf{e}_\beta \, \mathrm{d}A \right) - \langle \tilde{\mathbf{v}}_\beta \mathbf{e}_\beta \rangle \right\} \cdot \nabla \langle \omega_{A\beta} \rangle^\beta \right]
\end{aligned} \tag{44}$$

As with the momentum equation, we would like to obtain estimates of the closure variable terms in Eq. (44). On the basis of arguments presented in Appendix C, we will be able to neglect the time derivative term on the right-hand side relative to the left-hand side. The averaged mass continuity equation will thus become

$$\underbrace{\left(1+a_{\mathrm{v}}\varepsilon_{\beta}^{-1}\frac{k}{\left(1+K\langle\rho_{\mathrm{A}\beta}\rangle^{\beta}\right)^{2}}\right)}_{\text{Retardation}}\frac{\partial\langle\rho_{\mathrm{A}\beta}\rangle^{\beta}}{\partial t}$$
$$=\underbrace{-\nabla\cdot(\langle\mathbf{v}_{\beta}\rangle^{\beta}\langle\rho_{\mathrm{A}\beta}\rangle^{\beta})}_{\text{Advection}}+\underbrace{\varepsilon_{\beta}^{-1}\nabla\cdot\left[\mathbf{D}_{\beta}\cdot\nabla\langle\omega_{\mathrm{A}\beta}\rangle^{\beta}\right]}_{\text{Mechanical dispersion}}$$
$$+\underbrace{\nabla\cdot\left[\mathbf{D}_{\mathrm{eff}}\rho_{\beta}\cdot\nabla\langle\omega_{\mathrm{A}\beta}\rangle^{\beta}\right]}_{\text{Diffusion}}$$
$$+\underbrace{\varepsilon_{\beta}^{-1}\nabla\cdot\left[\left\{D_{\mathrm{AB}}\left(\frac{1}{V}\int_{A_{\beta\sigma}}\mathbf{n}_{\beta\sigma}\mathbf{d}_{\beta}\,\mathrm{d}A\right)-\langle\tilde{\mathbf{v}}_{\beta}\mathbf{d}_{\beta}\rangle\right\}\cdot\langle\mathbf{v}_{\beta}\rangle^{\beta}\right]}_{\text{Slip coupling effect}} \tag{45}$$

where

$$\mathbf{D}_{\mathrm{eff}}=D_{\mathrm{AB}}\varepsilon_{\beta}\left(\mathbf{I}+\rho_{\beta}^{-1}\frac{1}{V}\int_{A_{\beta\sigma}}\mathbf{n}_{\beta\sigma}\mathbf{e}_{\beta}\,\mathrm{d}A\right)$$

is the binary effective diffusivity and $\mathbf{D}_{\beta}=-\langle\tilde{\mathbf{v}}_{\beta}\mathbf{e}_{\beta}\rangle$ is the mechanical dispersion coefficient in the porous media of interest. The diffusion and dispersion terms are kept separate in Eq. (45) in order to explore an important caveat on the use of mechanical dispersion. We can utilize the estimate represented by Eq. (C.16) in order to obtain

$$\mathbf{D}_{\beta}=-\langle\tilde{\mathbf{v}}_{\beta}\mathbf{e}_{\beta}\rangle=\mathrm{O}(\langle\mathbf{v}_{\beta}\rangle^{\beta}\ell_{\beta}\langle\rho_{\beta}\rangle^{\beta}) \tag{46}$$

The mechanical dispersive term will be negligible compared with diffusive flux in many cases of gas flow in porous media based on

$$\text{Constraint:}\quad \frac{\langle\mathbf{v}_{\beta}\rangle^{\beta}\ell_{\beta}}{D_{\mathrm{AB}}}\ll 1 \tag{47}$$

This constraint is entirely consistent with dispersion criteria which have been well known, although often ignored, for many years [9,23–25]. Simply put, this constraint indicates that mechanical dispersion in a homogeneous porous medium will be negligible when the micro-scale Peclet number is less than one. We will retain mechanical dispersion in our formulation in order to preserve generality, with the understanding that in many situations of environmental concern it will be negligible.

The "slip coupling" term in Eq. (45) is the last remaining new term in the mass conservation equation. Again, we will explore its behavior through the use of order of magnitude estimates, the details of which are presented in Appendix C. We will utilize the estimate represented by Eq. (C.30b) (recognizing that at Peclet numbers significantly greatly than 1, the term represented by Eq. (C.30a) may be more dominant) in order to express the mass conservation equation for gas flow in porous media as

$$\underbrace{\left(1+a_{\mathrm{v}}\varepsilon_{\beta}^{-1}\frac{k}{\left(1+K\langle\rho_{\mathrm{A}\beta}\rangle^{\beta}\right)^{2}}\right)}_{\text{Retardation}}\frac{\partial\langle\rho_{\mathrm{A}\beta}\rangle^{\beta}}{\partial t}$$
$$=\underbrace{-\nabla\cdot(\langle\mathbf{v}_{\beta}\rangle^{\beta}\langle\rho_{\mathrm{A}\beta}\rangle^{\beta})}_{\text{Advection}}+\underbrace{\varepsilon_{\beta}^{-1}\nabla\cdot\left[\mathbf{D}_{\beta}\cdot\nabla\langle\omega_{\mathrm{A}\beta}\rangle^{\beta}\right]}_{\text{Mechanical dispersion}}$$
$$+\underbrace{\varepsilon_{\beta}^{-1}\nabla\cdot\left[\mathbf{D}_{\mathrm{eff}}\rho_{\beta}\cdot\nabla\langle\omega_{\mathrm{A}\beta}\rangle^{\beta}\right]}_{\text{Diffusion}}+\underbrace{\varepsilon_{\beta}^{-1}\nabla\cdot\left[\mathbf{R}_{\beta}\cdot\langle\mathbf{v}_{\beta}\rangle^{\beta}\right]}_{\text{Slip coupling effect}} \tag{48}$$

$\mathbf{R}_{\beta}=\mathrm{O}(\langle\rho_{\mathrm{A}\beta}\rangle^{\beta})$ is a term arising from the closure level coupling between mass and momentum which augments the traditional advective term. Expanding the intrinsic average velocity by utilizing Eq. (2) and assuming $\nabla\varepsilon_{\beta}=0$ leads to the final form of the volume averaged mass conservation equation

$$\underbrace{\left(\varepsilon_{\beta}+a_{\mathrm{v}}\frac{k}{\left(1+K\langle\rho_{\mathrm{A}\beta}\rangle^{\beta}\right)^{2}}\right)}_{\text{Retardation}}\frac{\partial\langle\rho_{\mathrm{A}\beta}\rangle^{\beta}}{\partial t}$$
$$=\underbrace{-\nabla\cdot\left(\langle\mathbf{v}_{\beta}\rangle\cdot\left(\mathbf{I}\langle\rho_{\mathrm{A}\beta}\rangle^{\beta}-\mathbf{R}_{\beta}\right)\right)}_{\text{Advection and slip coupling}}$$
$$+\underbrace{\nabla\cdot\left[\mathbf{D}_{\mathrm{eff}}\rho_{\beta}\cdot\nabla\langle\omega_{\mathrm{A}\beta}\rangle^{\beta}\right]}_{\text{Diffusion}}+\underbrace{\nabla\cdot\left[\mathbf{D}_{\beta}\cdot\nabla\langle\omega_{\mathrm{A}\beta}\rangle^{\beta}\right]}_{\text{Mechanical dispersion}} \tag{49}$$

4. Conclusions

Accounting for coupling between the gas-phase mass and momentum conservation equations at the closure level leads to non-traditional terms in the Darcy scale transport equations. The momentum equation for gas flow in porous media gains two new terms; the first due to the existence of a finite non-zero velocity at the gas–solid interface, the second due to the contribution of adsorption/desorption at the interface. The first of these conditions arises from inclusion of the slip velocity boundary condition at the micro-scale, the second stems from the closure level coupling with the mass equation. The mass transport equation contains a new term which arises due to coupling with the momentum equation. Estimates of this new term indicate that it may be quite significant relative to the traditional advective flux term. Order of magnitude estimates indicate that it may be significant in many gas flow regimes with significant advective fluxes. This new "slip coupling" flux term has a different functional form than the traditional mechanical dispersion term and it will be important in situations where mechanical dispersion is negligible (Peclet numbers less than one). In Part 2 we employ laboratory experiments and numerical models in order to explore the validity of these equations.

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Appendix A. Exploration of the point conservation equations

A.1. Point total momentum equations—simplification of the Navier–Stokes equation

The point momentum conservation equations can be restated as

$$0 = -\nabla p_\beta + \rho_\beta \mathbf{g} + \mu_\beta \nabla^2 \mathbf{v}_\beta \quad \text{in the } \beta\text{-phase} \tag{A.1a}$$

$$\text{B.C.1} \quad \mathbf{v}_\beta \cdot \mathbf{t}_{\beta\sigma} = v_{\text{slip}} = \frac{D_{AB}\mathbf{t}_{\beta\sigma} \cdot \nabla\omega_A}{\omega_A + \alpha} \quad \text{at } A_{\beta\sigma} \tag{A.1b}$$

$$\text{B.C.2} \quad \mathbf{v}_\beta \cdot \mathbf{n}_{\beta\sigma} = 0 \quad \text{at } A_{\beta\sigma} \tag{A.1c}$$

$$\text{B.C.3} \quad \mathbf{v}_\beta = \mathbf{f}(\mathbf{r}, t) \quad \text{at } A_{\beta e} \tag{A.1d}$$

The boundary condition represented by Eq. (A.1c) can be extracted from the following arguments. The Navier–Stokes equation (not restricted by the traditional incompressible fluid assumption) expressed as:

$$\frac{\partial}{\partial t}\rho_\beta \mathbf{v}_\beta + \nabla \cdot (\rho_\beta \mathbf{v}_\beta \mathbf{v}_\beta) = -\nabla p_\beta + \rho_\beta \mathbf{g} + \mu_\beta \nabla^2 \mathbf{v}_\beta \tag{A.2}$$

Taking the volume average of Eq. (A.2) and utilizing the spatial averaging theorem yields

$$\nabla \cdot \langle \rho_\beta \mathbf{v}_\beta \mathbf{v}_\beta \rangle + \frac{1}{V}\int_{A_{\beta\sigma}} \mathbf{n}_{\beta\sigma} \cdot (\rho_\beta \mathbf{v}_\beta \mathbf{v}_\beta)\,\mathrm{d}A = \frac{1}{V}\int_{V_\beta} \mu_\beta \nabla^2 \mathbf{v}_\beta \,\mathrm{d}V + \cdots \tag{A.3}$$

The term inside the area integral can be represented as

$$\mathbf{n}_{\beta\sigma} \cdot (\rho_\beta \mathbf{v}_\beta \mathbf{v}_\beta) = \mathbf{n}_{\beta\sigma} \cdot (\rho_{A\beta} \mathbf{v}_\beta \mathbf{v}_\beta) + \mathbf{n}_{\beta\sigma} \cdot (\rho_{B\beta} \mathbf{v}_\beta \mathbf{v}_\beta) \tag{A.4}$$

The second term on the right-hand side will be equal to zero if species "B" does not partition from the β-phase to the σ-phase. Thus, the area integral in Eq. (A.3) can be represented as

$$\frac{1}{V}\int_{A_{\beta\sigma}} \mathbf{n}_{\beta\sigma} \cdot (\rho_\beta \mathbf{v}_\beta \mathbf{v}_\beta)\,\mathrm{d}A = \frac{1}{V}\int_{A_{\beta\sigma}} \mathbf{n}_{\beta\sigma} \cdot (\rho_{A\beta} \mathbf{v}_\beta \mathbf{v}_\beta)\,\mathrm{d}A \tag{A.5}$$

The two integral terms in Eq. (A.3) thus be can be represented by the following estimates:

$$\frac{1}{V}\int_{A_{\beta\sigma}} \mathbf{n}_{\beta\sigma} \cdot (\rho_{A\beta} \mathbf{v}_\beta \mathbf{v}_\beta)\,\mathrm{d}A = \mathrm{O}\left(\frac{1}{\ell_\beta}\rho_\beta (\mathbf{v}_\beta^*)^2\right) \tag{A.6}$$

$$\frac{1}{V}\int_{V_\beta} \mu_\beta \nabla^2 \mathbf{v}_\beta \,\mathrm{d}V = \mathrm{O}\left(\varepsilon_\beta \mu_\beta \frac{\mathbf{v}_\beta}{\ell_\beta^2}\right) \tag{A.7}$$

The expression $\frac{1}{V}\int_{A_{\beta\sigma}} \mathbf{n}_{\beta\sigma}\,\mathrm{d}A$ is represented as a_v which can be estimated as ℓ_β^{-1} [9]. The characteristic velocity at the pore wall, $\mathbf{v}_\beta^*$, can be represented by the following estimate:

$$\mathbf{v}_\beta^* = \mathrm{O}\left(\frac{D_{AB}\left(\frac{\langle\omega_{A\beta}\rangle^\beta}{L}\right)}{1 - \langle\omega_{A\beta}\rangle^\beta}, \frac{D_{AB}\left(\frac{\langle\omega_{A\beta}\rangle^\beta}{L}\right)}{\langle\omega_{A\beta}\rangle^\beta + \alpha}\right) \tag{A.8}$$

The first term arises from the expression for the normal component developed in the mass averaging procedure (Eq. (A.33)). The second term follows from the tangential or slip velocity represented by Eq. (A.1b). We have estimated that changes in the mass fraction at the β–σ interface will be on the order of the average mass fraction and will occur over the large length scale L.

We can invoke the restriction

$$\frac{1}{V}\int_{A_{\beta\sigma}} \mathbf{n}_{\beta\sigma} \cdot (\rho_\beta \mathbf{v}_\beta \mathbf{v}_\beta)\,\mathrm{d}A \ll \frac{1}{V}\int_{V_\beta} \mu_\beta \nabla^2 \mathbf{v}_\beta \,\mathrm{d}V \tag{A.9a}$$

subject to

$$\text{Constraint:} \quad \langle\rho_\beta\rangle^\beta \left(\frac{D_{AB}\left(\frac{\langle\omega_{A\beta}\rangle^\beta}{L}\right)}{1 - \langle\omega_{A\beta}\rangle^\beta}, \frac{D_{AB}\left(\frac{\langle\omega_{A\beta}\rangle^\beta}{L}\right)}{\langle\omega_{A\beta}\rangle^\beta + \alpha}\right)^2 \ll \varepsilon_\beta \mu_\beta \frac{\langle\mathbf{v}_\beta\rangle^\beta}{\ell_\beta} \tag{A.9b}$$

With the idea that small causes give rise to small effects, the restriction represented by (A.9a) leads to the boundary condition

$$\text{B.C.2} \quad \mathbf{v}_\beta \cdot \mathbf{n}_{\beta\sigma} = 0 \quad \text{at } A_{\beta\sigma} \tag{A.10}$$

In other words, Eq. (A.10) is the non-trivial consequence of the restriction given by Eq. (A.9a). If the constraint represented by Eq. (A.9b) holds, $\mathbf{v}_\beta \cdot \mathbf{n}_{\beta\sigma}$ will have to become small at the β–σ interface in order for the left-hand side of Eq. (A.9a) to be small compared to the right-hand side. It is important to note that the contribution of the normal component of the advective velocity at the β–σ interface is negligible in the momentum conservation equation, but it may not be negligible in the mass conservation problem.

We would like to explore several of the assumptions which underlie the point momentum expressions, as represented by Eqs. (A.1). Eq. (A.2) can be simplified to

$$\nabla \cdot (\rho_\beta \mathbf{v}_\beta \mathbf{v}_\beta) = -\nabla p_\beta + \rho_\beta \mathbf{g} + \mu_\beta \nabla^2 \mathbf{v}_\beta \tag{A.11}$$

based on the constraint $\mu_\beta t^*/\rho_\beta \ell_\beta^2 \gg 1$ [3]. This constraint is consistent with the restriction $\rho\,\partial \mathbf{v}/\partial t \ll \mu \nabla^2 \mathbf{v}$ which indicates that the flow is quasi-steady. Eq. (A.11) can be at further simplified based on the restriction $\nabla \cdot (\rho_\beta \mathbf{v}_\beta \mathbf{v}_\beta) \ll \mu_\beta \nabla^2 \mathbf{v}_\beta$. Where we have utilized the estimates

$$\nabla \cdot (\rho_\beta \mathbf{v}_\beta \mathbf{v}_\beta) = \mathrm{O}\left(\langle \rho_\beta \rangle^\beta \frac{(\langle \mathbf{v}_\beta \rangle^\beta)^2}{\ell_\beta} \right) \tag{A.12}$$

$$\mu_\beta \nabla^2 \mathbf{v}_\beta = \mathrm{O}\left(\mu_\beta \frac{\langle \mathbf{v}_\beta \rangle^\beta}{\ell_\beta^2} \right) \tag{A.13}$$

$$\text{Constraint:} \quad \frac{\langle \rho_\beta \rangle^\beta \langle \mathbf{v}_\beta \rangle^\beta \ell_\beta}{\mu_\beta} \ll 1 \tag{A.14}$$

Yielding

$$0 = -\nabla p_\beta + \rho_\beta \mathbf{g} + \mu_\beta \nabla^2 \mathbf{v}_\beta \tag{A.15}$$

The estimates indicated by Eqs. (A.12) and (A.13) are based on the idea that the changes in the point velocity will be on the order of the average and that they will occur over the small length-scale ℓ_β.

A.2. Point total mass equation—condition of incompressibility

$$\nabla \cdot \mathbf{v}_\beta = 0 \quad \text{in the } \beta\text{-phase} \tag{A.16}$$

The condition of incompressibility represent by Eq. (A.16) can be obtained by starting with the total mass conservation equation

$$\frac{\partial \rho_\beta}{\partial t} + \nabla \cdot (\mathbf{v}_\beta \rho_\beta) = 0 \tag{A.17}$$

This can be rearranged to yield

$$\nabla \cdot \mathbf{v}_\beta = -\rho_\beta^{-1} \frac{\partial \rho_\beta}{\partial t} - \rho_\beta^{-1} \mathbf{v}_\beta \cdot \nabla \rho_\beta \tag{A.18}$$

The following order of magnitude estimates can be made for each of the terms in Eq. (A.18):

$$\nabla \cdot \mathbf{v}_\beta = \mathrm{O}\left(\frac{\langle \mathbf{v}_\beta \rangle^\beta}{\ell_\beta} \right) \tag{A.19a}$$

$$\rho_\beta^{-1} \frac{\partial \rho_\beta}{\partial t} = \mathrm{O}\left(\frac{\Delta \rho_\beta}{\rho_\beta t^*} \right) \tag{A.19b}$$

$$\rho_\beta^{-1} \mathbf{v}_\beta \cdot \nabla \rho_\beta = \mathrm{O}\left(\frac{\Delta \rho_\beta}{\rho_\beta L} \langle \mathbf{v}_\beta \rangle^\beta \right) \tag{A.19c}$$

The estimates employed in Eqs. (A.19) are based on arguments presented above. The gradient of the velocity on the left hand side of Eq. (A.18) will be the dominant with respect to each of the individual terms on the right-hand side subject to

$$\text{Constraint:} \quad \langle \mathbf{v}_\beta \rangle^\beta \gg \frac{\Delta \rho_\beta}{\rho_\beta} \frac{\ell_\beta}{t^*} \tag{A.20}$$

$$\text{Constraint:} \quad \frac{\Delta \rho_\beta}{\rho_\beta} \frac{\ell_\beta}{L} \ll 1 \tag{A.21}$$

Eq. (A.17) thus becomes

$$\nabla \cdot \mathbf{v}_\beta = 0 \tag{A.20}$$

A.3. Point mass equations—sorptive boundary condition

Focusing on the first boundary condition in the point mass conservation equations (Eq. (6b)), we may utilize Fick's Law in order to obtain

$$\text{B.C.1} \quad \mathbf{n}_{\beta\sigma} \cdot (\rho_{A\beta} \mathbf{v}_\beta - \rho_\beta D_{AB} \nabla \omega_{A\beta}) = \frac{\partial \rho_{AS}}{\partial t} \quad \text{at } A_{\beta\sigma} \tag{A.22}$$

We would like to be able to express this boundary condition in terms of $\rho_{A\beta}$. If the surface sorption depends on the number of vacant sites and the number of vacant sites can be expressed as linear function of the surface density (the conditions for the Langmuir–Hinshelwood formulation) we can express the net rate of adsorption (in the absence of surface reaction and transport) as [9]

$$\frac{\partial \rho_{AS}}{\partial t} = (k_1 - K^* \rho_{AS}) \rho_{A\beta} - k_{-1} \rho_{AS} \tag{A.23}$$

where ρ_{AS} is the density of species A at the adsorbing surface (for addition details see [26]). If we assume local sorptive equilibrium, Eq. (A.23) becomes

$$0 = (k_1 - K^* \rho_{AS}) \rho_{A\beta}^{eq} - k_{-1} \rho_{AS} \tag{A.24}$$

where $\rho_{A\beta}^{eq}$ is the equilibrium species A density in the β-phase. Eq. (A.24) is equivalent to

$$(k_{-1} + K^* \rho_{A\beta}^{eq}) \rho_{AS} = k_1 \rho_{A\beta}^{eq} \tag{A.25}$$

Defining the constants $k = k_1/k_{-1}$, and $K = K^*/k_{-1}$, the surface density may be expressed as

$$\rho_{AS} = \frac{k \rho_{A\beta}^{eq}}{1 + K \rho_{A\beta}^{eq}} \tag{A.26}$$

This is equivalent to a Langmuir sorption isotherm. Taking the derivative with respect to time and using the local equilibrium assumption, $\rho_{A\beta}^{eq} = \rho_{A\beta}$, yields

$$\frac{\partial \rho_{AS}}{\partial t} = \frac{k}{(1+K\rho_{A\beta})^2}\frac{\partial \rho_{A\beta}}{\partial t} \quad \text{at } A_{\beta\sigma} \tag{A.27}$$

Substituting this expression into B.C.1 gives

$$\text{B.C.1} \quad \mathbf{n}_{\beta\sigma}\cdot(\rho_{A\beta}\mathbf{v}_\beta - \rho_\beta D_{AB}\nabla\omega_{A\beta}) = \frac{k}{(1+K\rho_{A\beta})^2}\frac{\partial \rho_{A\beta}}{\partial t} \quad \text{at } A_{\beta\sigma} \tag{A.28}$$

In the traditional derivation of the volume averaged mass conservation equation, the assumption $\mathbf{n}_{\beta\sigma}\cdot\mathbf{v}_\beta = 0$ is utilized in order to simplify the form of this boundary condition. We would like to examine this assumption and determine its range of validity. The advective term in Eq. (A.28) can be represented (for a binary system) as

$$\mathbf{n}_{\beta\sigma}\cdot\rho_{A\beta}\mathbf{v}_\beta = \rho_{A\beta}(\omega_{A\beta}\mathbf{v}_{A\beta} + \omega_{B\beta}\mathbf{v}_{B\beta})\cdot\mathbf{n}_{\beta\sigma} \tag{A.29}$$

where $\mathbf{v}_{A\beta}$ and $\mathbf{v}_{B\beta}$ are the species velocities of the components of the system. For the case where component B does not partition from the β-phase to the σ-phase (as is often assumed for air, for example)

$$\mathbf{v}_{B\beta}\cdot\mathbf{n}_{\beta\sigma} = 0 \quad \text{at } A_{\beta\sigma} \tag{A.30}$$

Eq. (A.29) can thus be expressed as

$$\mathbf{n}_{\beta\sigma}\cdot\rho_{A\beta}\mathbf{v}_\beta = \rho_{A\beta}\left(\omega_{A\beta}\mathbf{v}_\beta + \frac{\rho_{A\beta}\mathbf{u}_{A\beta}}{\rho_\beta}\right)\cdot\mathbf{n}_{\beta\sigma} \tag{A.31}$$

where $\mathbf{u}_{A\beta}$ is the diffusive velocity of species A. The diffusive flux of species A, $\rho_{A\beta}\mathbf{u}_{A\beta}$, can be expressed equivalently, using Fick's Law, to yield

$$\mathbf{n}_{\beta\sigma}\cdot\rho_{A\beta}\mathbf{v}_\beta = \rho_{A\beta}\left(\omega_{A\beta}\mathbf{v}_\beta - \frac{\rho_\beta D_{A\beta}\nabla\omega_{A\beta}}{\rho_\beta}\right)\cdot\mathbf{n}_{\beta\sigma} \tag{A.32}$$

Eq. (A.32) is equivalent to

$$\mathbf{n}_{\beta\sigma}\cdot\rho_{A\beta}\mathbf{v}_\beta = -\mathbf{n}_{\beta\sigma}\cdot\left[\left(\frac{\omega_{A\beta}}{1-\omega_{A\beta}}\right)\rho_\beta D_{AB}\nabla\omega_{A\beta}\right] \tag{A.33}$$

This expression clearly demonstrates that the assumption $\mathbf{n}_{\beta\sigma}\cdot\mathbf{v}_\beta = 0$ will only be valid at the β–σ interface when the constraint $(\omega_{A\beta}/1-\omega_{A\beta}) \ll 1$ is met. In order preserve the generality of our equations, we will not restrict our analysis to this case. Substituting Eq. (A.33) into Eq. (A.28) gives

$$\mathbf{n}_{\beta\sigma}\cdot\left[-\left(\frac{\omega_{A\beta}}{1-\omega_{A\beta}}\right)\rho_\beta D_{AB}\nabla\omega_{A\beta} - \rho_\beta D_{AB}\nabla\omega_{A\beta}\right] = \frac{k}{(1+K\rho_{A\beta})^2}\frac{\partial \rho_{A\beta}}{\partial t} \quad \text{at } A_{\beta\sigma} \tag{A.34}$$

After algebraic manipulation of the left-hand side, this yields the boundary condition

$$\text{B.C.1} \quad -\mathbf{n}_{\beta\sigma}\cdot\left(\frac{\rho_\beta D_{AB}\nabla\omega_{A\beta}}{1-\omega_{A\beta}}\right) = \frac{k}{(1+K\rho_{A\beta})^2}\frac{\partial \rho_{A\beta}}{\partial t} \quad \text{at } A_{\beta\sigma} \tag{A.35a}$$

or equivalently

$$\text{B.C.1} \quad -\mathbf{n}_{\beta\sigma}\cdot\rho_\beta D_{AB}\nabla\omega_{A\beta} = \frac{(1-\omega_{A\beta})k}{(1+K\rho_{A\beta})^2}\frac{\partial \rho_{A\beta}}{\partial t} \quad \text{at } A_{\beta\sigma} \tag{A.35b}$$

Appendix B. Volume averaging

B.1. Mass conservation equations

B.1.1. Sorptive terms

We can utilize the decomposition $\rho_{A\beta} = \langle\rho_{A\beta}\rangle^\beta + \tilde{\rho}_{A\beta}$ to expand the sorption isotherm term in Eq. (13) as

$$\frac{k}{(1+K\rho_{A\beta})^2} = k\left[1+2K(\langle\rho_{A\beta}\rangle^\beta + \tilde{\rho}_{A\beta}) + K^2\left(\tilde{\rho}_{A\beta}^2 + 2\langle\rho_{A\beta}\rangle^\beta\tilde{\rho}_{A\beta} + \left(\langle\rho_{A\beta}\rangle^\beta\right)^2\right)\right]^{-1} \tag{B.1}$$

Combining the deviation terms yields

$$\frac{k}{(1+K\rho_{A\beta})^2} = k\left[1+2K\langle\rho_{A\beta}\rangle^\beta + K^2(\langle\rho_{A\beta}\rangle^\beta)^2 + \tilde{\rho}_{A\beta}\left(2K+2K^2\langle\rho_{A\beta}\rangle^\beta\right) + K^2\tilde{\rho}_{A\beta}^2\right]^{-1} \tag{B.2}$$

We would like to simplify this expression as much as possible in order to more easily utilize it in our averaged equation. If we define function $H(\langle\rho_{A\beta}\rangle^\beta, \tilde{\rho}_{A\beta})$ as the right-hand side of Eq. (B.2) we can express it as a Taylor series expanded around $\tilde{\rho}_{A\beta} = 0$

$$H(\langle\rho_{A\beta}\rangle^\beta, \tilde{\rho}_{A\beta}) = H(\langle\rho_{A\beta}\rangle^\beta, 0) + \tilde{\rho}_{A\beta}\frac{\partial H(\langle\rho_{A\beta}\rangle^\beta, 0)}{\partial\tilde{\rho}_{A\beta}} + \frac{\tilde{\rho}_{A\beta}^2}{2}\frac{\partial^2 H(\langle\rho_{A\beta}\rangle^\beta, 0)}{\partial\tilde{\rho}_{A\beta}^2} + \cdots \tag{B.3}$$

We can express $H(\langle\rho_{A\beta}\rangle^\beta, 0)$ and its derivatives as

$$H(\langle\rho_{A\beta}\rangle^\beta, 0) = k\left[1+2K\langle\rho_{A\beta}\rangle^\beta + K^2(\langle\rho_{A\beta}\rangle^\beta)^2\right]^{-1} \tag{B.4a}$$

$$\frac{\partial H(\langle\rho_{A\beta}\rangle^\beta, 0)}{\partial\tilde{\rho}_{A\beta}} = -k\left[1+2K\langle\rho_{A\beta}\rangle^\beta + K^2(\langle\rho_{A\beta}\rangle^\beta)^2\right]^{-2} \times (2K+2K^2\langle\rho_{A\beta}\rangle^\beta) \tag{B.4b}$$

$$\frac{\partial^2 H\left(\langle\rho_{A\beta}\rangle^\beta, 0\right)}{\partial\tilde{\rho}_{A\beta}^2} = 6kK^2\left[1+2K\langle\rho_{A\beta}\rangle^\beta + K^2(\langle\rho_{A\beta}\rangle^\beta)^2\right]^{-2} \tag{B.4c}$$

Defining $\Gamma = \left[1 + 2K\langle\rho_{A\beta}\rangle^{\beta} + K^2(\langle\rho_{A\beta}\rangle^{\beta})^2\right]^{-1}$ we can express Eq. (B.3) as

$$H(\langle\rho_{A\beta}\rangle^{\beta}, \tilde{\rho}_{A\beta}) = k\Gamma - \tilde{\rho}_{A\beta}(2K + 2K^2\langle\rho_{A\beta}\rangle^{\beta})k\Gamma^2 + 3\tilde{\rho}^2_{A\beta}K^2K\Gamma^2 + \cdots \tag{B.5}$$

We can now proceed with simplifications to this expression. The third term on the right-hand side can be eliminated by employing the estimate and constraint represented by Eqs. (10) and (11). The third term on the right-hand side of Eq. (B.5) will be negligible compared to the first term on the right-hand side if the following holds:

$$\text{Constraint:} \quad \frac{3\left(\langle\rho_{A\beta}\rangle^{\beta}\right)^2(\ell_\beta/L)^2K^2}{\left[1 + 2K\langle\rho_{A\beta}\rangle^{\beta} + (\langle\rho_{A\beta}\rangle^{\beta})^2\right]} \ll 1 \tag{B.6}$$

In order to demonstrate the utility of the constraint represented by Eq. (B.6), we can examine simplifications of the constraint for specific values of $\langle\rho_{A\beta}\rangle^{\beta}$ and K. For $\langle\rho_{A\beta}\rangle^{\beta} \ll 1$ kg/m^3 and $K = O(1)$ m^3/kg the constraint represented by Eq. (B.6) will reduce to $3(\langle\rho_{A\beta}\rangle^{\beta})^2 \times (\ell_\beta/L)^2 \ll 1$. For $\langle\rho_{A\beta}\rangle^{\beta} = O(1)$ kg/m^3 and $K = O(1)$ m^3/kg the constraint will become $\ell_\beta \ll (2/\sqrt{3})L$.

Similarly, the second term on the right-hand side of Eq. (B.5) can be discarded with respect to the first term on the right-hand side if the following holds:

$$\text{Constraint:} \quad \frac{\langle\rho_{A\beta}\rangle^{\beta}(\ell_\beta/L)(2K + 2K^2\langle\rho_{A\beta}\rangle^{\beta})}{1 + 2K\langle\rho_{A\beta}\rangle^{\beta} + K^2(\langle\rho_{A\beta}\rangle^{\beta})^2} \ll 1 \tag{B.7}$$

As with the previous constraint we can utilize particular values of $\langle\rho_{A\beta}\rangle^{\beta}$ and K in order to examine the validity of Eq. (B.7). For $\langle\rho_{A\beta}\rangle^{\beta} \ll 1$ kg/m^3 and $K = O(1)$ m^3/kg the constraint represented by Eq. (B.7) will reduce to $\langle\rho_{A\beta}\rangle^{\beta}\ell_\beta/L \lll 1$. For $\langle\rho_{A\beta}\rangle^{\beta} = O(1)$ kg/m^3 L and $K = O(1)$ m^3/kg the constraint will become $\ell_\beta \ll L$. On the basis of these simplifications we can express Eq. (B.1) as

$$\frac{k}{(1 + K\rho_{A\beta})^2} = k\left[1 + 2K\langle\rho_{A\beta}\rangle^{\beta} + K^2\left(\langle\rho_{A\beta}\rangle^{\beta}\right)^2\right]^{-1}$$

or, equivalently

$$\frac{k}{(1 + K\rho_{A\beta})^2} = \frac{k}{\left(1 + K\langle\rho_{A\beta}\rangle^{\beta}\right)^2} \tag{B.8}$$

B.1.2. Development of the mass conservation closure problem

The closure problem will be set up by first subtracting the unclosed averaged mass conservation equation

$$\begin{aligned}\frac{\partial\langle\rho_{A\beta}\rangle^{\beta}}{\partial t} &= -\nabla\cdot\left(\langle\mathbf{v}_\beta\rangle^{\beta}\langle\rho_{A\beta}\rangle^{\beta}\right) - \varepsilon_\beta^{-1}\nabla\cdot\langle\tilde{\rho}_{A\beta}\tilde{\mathbf{v}}_\beta\rangle \\ &\quad + \varepsilon_\beta^{-1}\nabla\cdot\left(D_{AB}\rho_\beta\varepsilon_\beta\nabla\langle\omega_{A\beta}\rangle^{\beta}\right) \\ &\quad + \varepsilon_\beta^{-1}\nabla\cdot\left(D_{AB}\rho_\beta\frac{1}{V}\int_{A_{\beta\sigma}}\mathbf{n}_{\beta\sigma}\tilde{\omega}_{A\beta}\,dA\right) \\ &\quad - a_v\varepsilon_\beta^{-1}\frac{k}{\left(1 + K\langle\rho_{A\beta}\rangle^{\beta}\right)^2}\frac{\partial\langle\rho_{A\beta}\rangle^{\beta}}{\partial t}\end{aligned} \tag{B.9}$$

from the point equation

$$\frac{\partial\rho_{A\beta}}{\partial t} = -\nabla\cdot(\mathbf{v}_\beta\rho_{A\beta}) + \nabla\cdot(\rho_\beta D_{AB}\nabla\omega_{A\beta}) \tag{B.10}$$

in order to obtain

$$\begin{aligned}\frac{\partial\tilde{\rho}_{A\beta}}{\partial t} &= -\nabla\cdot(\mathbf{v}_\beta\rho_{A\beta}) + \nabla\cdot\left(\langle\mathbf{v}_\beta\rangle^{\beta}\langle\rho_{A\beta}\rangle^{\beta}\right) \\ &\quad + \varepsilon_\beta^{-1}\nabla\cdot\langle\tilde{\mathbf{v}}_\beta\tilde{\rho}_{A\beta}\rangle + \nabla\cdot\left(\rho_\beta D_{AB}\nabla\langle\omega_{A\beta}\rangle^{\beta}\right) \\ &\quad + \nabla\cdot(\rho_\beta D_{AB}\nabla\tilde{\omega}_{A\beta}) - \varepsilon_\beta^{-1}\nabla\cdot\left(D_{AB}\rho_\beta\varepsilon_\beta\nabla\langle\omega_{A\beta}\rangle^{\beta}\right) \\ &\quad - \varepsilon_\beta^{-1}\nabla\cdot\left(D_{AB}\rho_\beta\frac{1}{V}\int_{A_{\beta\sigma}}\mathbf{n}_{\beta\sigma}\tilde{\omega}_{A\beta}\,dA\right) \\ &\quad + a_v\varepsilon_\beta^{-1}\frac{k}{\left(1 + K\langle\rho_{A\beta}\rangle^{\beta}\right)^2}\frac{\partial\langle\rho_{A\beta}\rangle^{\beta}}{\partial t}\end{aligned} \tag{B.11a}$$

$$\begin{aligned}\text{B.C.1} \quad -\mathbf{n}_{\beta\sigma}\cdot(\rho_\beta D_{AB}\nabla\tilde{\omega}_{A\beta}) &= \mathbf{n}_{\beta\sigma}\cdot\left(\rho_\beta D_{AB}\nabla\langle\omega_{A\beta}\rangle^{\beta}\right) \\ &\quad + \frac{k\left(1 - \langle\omega_{A\beta}\rangle^{\beta}\right)}{\left(1 + K\langle\rho_{A\beta}\rangle^{\beta}\right)^2}\frac{\partial\tilde{\rho}_{A\beta}}{\partial t} \\ &\quad + \frac{k\left(1 - \langle\omega_{A\beta}\rangle^{\beta}\right)}{\left(1 + K\langle\rho_{A\beta}\rangle^{\beta}\right)^2}\frac{\partial\langle\rho_{A\beta}\rangle^{\beta}}{\partial t} \quad \text{at } A_{\beta\sigma}\end{aligned} \tag{B.11b}$$

$$\text{B.C.2} \quad \tilde{\rho}_{A\beta} = f(\mathbf{r}, t) \quad \text{at } A_{\beta e} \tag{B.11c}$$

$$\text{I.C.} \quad \tilde{\rho}_{A\beta} = g(\mathbf{r}), \quad t = 0 \tag{B.11d}$$

where we have decomposed the boundary condition given by Eq. (22b).

We can now proceed with simplifications to Eqs. (B.11a) and (B.11b). As in the derivation of the volume averaged equations, we will develop estimates of various terms in the equations of interest and eliminate those terms which can be neglected on the basis of reasonable constraints on the system. First we will focus on the "local diffusion" term in Eq. (B.11a) and make the estimates

$$\varepsilon_\beta^{-1}\nabla\cdot\left(D_{AB}\rho_\beta\frac{1}{V}\int_{A_{\beta\sigma}}\mathbf{n}_{\beta\sigma}\tilde{\omega}_{A\beta}\,dA\right)=O\left(\frac{\Delta\rho_\beta\tilde{\omega}_{A\beta}D_{AB}\varepsilon_\beta^{-1}}{L\ell_\beta}\right)\tag{B.12}$$

$$\nabla\cdot(\rho_\beta D_{AB}\nabla\tilde{\omega}_{A\beta})=O\left(\frac{\rho_\beta D_{AB}\tilde{\omega}_{A\beta}}{\ell_\beta^2}\right)\tag{B.13}$$

The gradient of the area integral will be associated with a macro-length-scale, L. As described in Appendix A, the area integral term will be estimated by ℓ_β^{-1}. Employing these estimates we can neglect the local "diffusion" term relative to $\nabla\cdot(\rho_\beta D_{AB}\nabla\tilde{\omega}_{A\beta})$, subject to

$$\text{Constraint:}\quad \frac{\Delta\rho_\beta}{\rho_\beta}\frac{\ell_\beta}{L}\ll\varepsilon_\beta\tag{B.14}$$

The volume diffusive source $\varepsilon_\beta^{-1}\nabla\cdot(D_{AB}\rho_\beta\varepsilon_\beta\nabla\langle\omega_{A\beta}\rangle^\beta)$ can be neglected relative to the surface diffusive source $\mathbf{n}_{\beta\sigma}\cdot(\rho_\beta D_{AB}\nabla\langle\omega_{A\beta}\rangle^\beta)$ following Whitaker [9, Section 1.4.2] subject to:

$$\text{Constraint:}\quad \frac{\text{volume source \# 1}}{\text{surface source}}=O\left(\frac{\ell_\beta}{L}\Delta\varepsilon_\beta\right)\ll 1\tag{B.15}$$

Employing the estimates

$$\frac{1}{V}\int_{A_{\beta\sigma}}\mathbf{n}_{\beta\sigma}\cdot\left(\rho_\beta D_{AB}\nabla\langle\omega_{A\beta}\rangle^\beta\right)dA=O\left(a_v\rho_\beta D_{AB}\nabla\langle\omega_{A\beta}\rangle^\beta\right)\tag{B.16}$$

$$\frac{1}{V}\int_{V_\beta}\left[\nabla\cdot\left(\rho_\beta D_{AB}\nabla\langle\omega_{A\beta}\rangle^\beta\right)\right]dV=O\left(\frac{\varepsilon_\beta\rho_\beta D_{AB}\nabla\langle\omega_{A\beta}\rangle^\beta}{L}\right)\tag{B.17}$$

and invoking similar arguments we will can eliminate $\frac{1}{V}\int_{V_\beta}[\nabla\cdot(\rho_\beta D_{AB}\nabla\langle\omega_{A\beta}\rangle^\beta)]dV$ relative to $\frac{1}{V}\int_{A_{\beta\sigma}}\mathbf{n}_{\beta\sigma}\cdot(\rho_\beta D_{AB}\nabla\langle\omega_{A\beta}\rangle^\beta)dA$, subject to

$$\text{Constraint:}\quad \frac{\text{volume source \# 2}}{\text{surface source}}=O\left(\frac{\varepsilon_\beta\ell_\beta}{L}\right)\ll 1\tag{B.18}$$

where we have assumed that $a_v=O(\ell_\beta^{-1})$ (see [9, Chapter 1]). The above simplifications allow us to express the closure Eq. (B.11a) as

$$\begin{aligned}\frac{\partial\tilde{\rho}_{A\beta}}{\partial t}&=-\nabla\cdot(\mathbf{v}_\beta\rho_{A\beta})+\nabla\cdot\left(\langle\mathbf{v}_\beta\rangle^\beta\langle\rho_{A\beta}\rangle^\beta\right)\\&\quad+\varepsilon_\beta^{-1}\nabla\cdot\langle\tilde{\mathbf{v}}_\beta\tilde{\rho}_{A\beta}\rangle+\nabla\cdot(\rho_\beta D_{AB}\nabla\tilde{\omega}_{A\beta})\\&\quad+a_v\varepsilon_\beta^{-1}\frac{k}{\left(1+K\langle\rho_{A\beta}\rangle^\beta\right)^2}\frac{\partial\langle\rho_{A\beta}\rangle^\beta}{\partial t}\end{aligned}\tag{B.19}$$

The first two terms on the right-hand side of Eq. (B.19) can be expanded as

$$\begin{aligned}&-\nabla\cdot(\mathbf{v}_\beta\rho_{A\beta})+\nabla\cdot\left(\langle\mathbf{v}_\beta\rangle^\beta\langle\rho_{A\beta}\rangle^\beta\right)\\&\quad=-\langle\mathbf{v}_\beta\rangle^\beta\cdot\nabla\langle\rho_{A\beta}\rangle^\beta-\langle\rho_{A\beta}\rangle^\beta\nabla\cdot\langle\mathbf{v}_\beta\rangle^\beta\\&\qquad-\nabla\cdot\left(\tilde{\mathbf{v}}_\beta\langle\rho_{A\beta}\rangle^\beta\right)-\mathbf{v}_\beta\cdot\nabla\tilde{\rho}_{A\beta}-\tilde{\rho}_{A\beta}\nabla\cdot\mathbf{v}_\beta\\&\qquad+\langle\mathbf{v}_\beta\rangle^\beta\cdot\nabla\langle\rho_{A\beta}\rangle^\beta+\langle\rho_{A\beta}\rangle^\beta\nabla\cdot\langle\mathbf{v}_\beta\rangle^\beta\end{aligned}\tag{B.20a}$$

or equivalently

$$\begin{aligned}&-\nabla\cdot(\mathbf{v}_\beta\rho_{A\beta})+\nabla\cdot\left(\langle\mathbf{v}_\beta\rangle^\beta\langle\rho_{A\beta}\rangle^\beta\right)\\&\quad=-\nabla\cdot\left(\tilde{\mathbf{v}}_\beta\langle\rho_{A\beta}\rangle^\beta\right)-\nabla\cdot(\mathbf{v}_\beta\tilde{\rho}_{A\beta})\end{aligned}\tag{B.20b}$$

The closure equation thus becomes

$$\begin{aligned}\frac{\partial\tilde{\rho}_{A\beta}}{\partial t}&=-\nabla\cdot\left(\tilde{\mathbf{v}}_\beta\langle\rho_{A\beta}\rangle^\beta\right)-\nabla\cdot(\mathbf{v}_\beta\tilde{\rho}_{A\beta})\\&\quad+\varepsilon_\beta^{-1}\nabla\cdot\langle\tilde{\mathbf{v}}_\beta\tilde{\rho}_{A\beta}\rangle+\nabla\cdot(\rho_\beta D_{AB}\nabla\tilde{\omega}_{A\beta})\\&\quad+a_v\varepsilon_\beta^{-1}\frac{k}{\left(1+K\langle\rho_{A\beta}\rangle^\beta\right)^2}\frac{\partial\langle\rho_{A\beta}\rangle^\beta}{\partial t}\end{aligned}\tag{B.21}$$

The estimates

$$\varepsilon_\beta^{-1}\nabla\cdot\langle\tilde{\mathbf{v}}_\beta\tilde{\rho}_{A\beta}\rangle=O\left(\langle\mathbf{v}_\beta\rangle^\beta\frac{\tilde{\rho}_{A\beta}}{L}\right)\tag{B.22}$$

$$\nabla\cdot(\mathbf{v}_\beta\tilde{\rho}_{A\beta})=O\left(\langle\mathbf{v}_\beta\rangle^\beta\frac{\tilde{\rho}_{A\beta}}{\ell_\beta}\right)\tag{B.23}$$

have disparate length-scales due to the fact that the term in Eq. (B.22) contains the divergence of an macro-scale quantity, while in Eq. (B.23) we are taking the divergence of micro-scale quantities. We will neglect $\varepsilon_\beta^{-1}\nabla\cdot\langle\tilde{\mathbf{v}}_\beta\tilde{\rho}_{A\beta}\rangle$ relative to $\nabla\cdot\langle\mathbf{v}_\beta\tilde{\rho}_{A\beta}\rangle$ based on

$$\text{Constraint:}\quad \ell_\beta\ll L\tag{B.24}$$

The closure equation is thus simplified to

$$\begin{aligned}\frac{\partial\tilde{\rho}_{A\beta}}{\partial t}&=-\nabla\cdot\left(\tilde{\mathbf{v}}_\beta\langle\rho_{A\beta}\rangle^\beta\right)-\nabla\cdot(\tilde{\mathbf{v}}_\beta\tilde{\rho}_{A\beta})\\&\quad+\nabla\cdot(\rho_\beta D_{AB}\nabla\tilde{\omega}_{A\beta})+a_v\varepsilon_\beta^{-1}\frac{k}{\left(1+K\langle\rho_{A\beta}\rangle^\beta\right)^2}\frac{\partial\langle\rho_{A\beta}\rangle^\beta}{\partial t}\end{aligned}\tag{B.25}$$

We will now examine the constraints associated with assuming that the closure problem is quasi-steady. The first step is to employ the estimates

$$\frac{\partial \tilde{\rho}_{A\beta}}{\partial t} = \mathrm{O}\left(\frac{\tilde{\rho}_{A\beta}}{t^*}\right) \tag{B.26}$$

$$\nabla \cdot (\rho_\beta \mathscr{D}_{AB} \nabla \tilde{\omega}_{A\beta}) = \mathrm{O}\left(\frac{\mathscr{D}_{AB}\tilde{\rho}_{A\beta}}{\ell_\beta^2}\right) \tag{B.27}$$

The closure equation will be quasi-steady if $\nabla \cdot (\rho_\beta \mathscr{D}_{AB} \nabla \tilde{\omega}_{A\beta}) \gg \partial \tilde{\rho}_{A\beta}/\partial t$, which implies

$$\text{Constraint:} \quad \frac{\mathscr{D}_{AB} t^*}{\ell_\beta^2} \gg 1 \tag{B.28}$$

The simplified closure equation can be expressed as

$$\nabla \cdot \left(\tilde{\mathbf{v}}_\beta \langle \rho_{A\beta}\rangle^\beta\right) + \nabla \cdot (\mathbf{v}_\beta \tilde{\rho}_{A\beta}) = \nabla \cdot (\rho_\beta \mathscr{D}_{AB} \nabla \tilde{\omega}_{A\beta}) + a_v \varepsilon_\beta^{-1} \frac{k}{\left(1 + K\langle \rho_{A\beta}\rangle^\beta\right)^2} \frac{\partial \langle \rho_{A\beta}\rangle^\beta}{\partial t} \tag{B.29a}$$

$$\text{B.C.1} \quad -\mathbf{n}_{\beta\sigma} \cdot (\rho_\beta \mathscr{D}_{AB} \nabla \tilde{\omega}_{A\beta}) = \mathbf{n}_{\beta\sigma} \cdot \left(\rho_\beta \mathscr{D}_{AB} \nabla \langle \omega_{A\beta}\rangle^\beta\right) + \frac{k\left(1 - \langle \omega_{A\beta}\rangle^\beta\right)}{\left(1 + K\langle \rho_{A\beta}\rangle^\beta\right)^2} \frac{\partial \tilde{\rho}_{A\beta}}{\partial t} + \frac{k\left(1 - \langle \omega_{A\beta}\rangle^\beta\right)}{\left(1 + K\langle \rho_{A\beta}\rangle^\beta\right)^2} \frac{\partial \langle \rho_{A\beta}\rangle^\beta}{\partial t} \quad \text{at } A_{\beta\sigma} \tag{B.29b}$$

Similarly, the boundary condition will be quasi-steady if the second term on the right-hand side of Eq. (B.29b) can be neglected relative to the term on the left-hand side, subject to

$$\text{Constraint:} \quad \frac{\mathscr{D}_{AB} t^* \left(1 + K\langle \rho_{A\beta}\rangle^\beta\right)^2}{\ell_\beta k \left(1 - \langle \omega_{A\beta}\rangle^\beta\right)} \gg 1 \tag{B.30}$$

The quasi-steady boundary condition is thus

$$\text{B.C.1} \quad -\mathbf{n}_{\beta\sigma} \cdot (\rho_\beta \mathscr{D}_{AB} \nabla \tilde{\omega}_{A\beta}) = \mathbf{n}_{\beta\sigma} \cdot \left(\rho_\beta \mathscr{D}_{AB} \nabla \langle \omega_{A\beta}\rangle^\beta\right) + \frac{k\left(1 - \langle \omega_{A\beta}\rangle^\beta\right)}{\left(1 + K\langle \rho_{A\beta}\rangle^\beta\right)^2} \frac{\partial \langle \rho_{A\beta}\rangle^\beta}{\partial t} \quad \text{at } A_{\beta\sigma} \tag{B.31}$$

In order to simplify the solution of the closure problem all terms containing $\langle \omega_{A\beta}\rangle^\beta$ and $\tilde{\omega}_{A\beta}$ in the governing equation and the boundary condition need to be expressed in terms of $\langle \rho_{A\beta}\rangle^\beta$, $\tilde{\rho}_{A\beta}$, and $\langle \rho_\beta\rangle^\beta$. The first step is to express the mass fraction in the following manner:

$$\omega_{A\beta} = \frac{\rho_{A\beta}}{\rho_\beta} = \frac{\langle \rho_{A\beta}\rangle^\beta + \tilde{\rho}_{A\beta}}{\langle \rho_\beta\rangle^\beta + \tilde{\rho}_\beta} \tag{B.32}$$

and then define

$$\langle \omega_{A\beta}\rangle^\beta = \frac{\langle \rho_{A\beta}\rangle^\beta}{\langle \rho_\beta\rangle^\beta + \tilde{\rho}_\beta} \quad \text{and} \quad \tilde{\omega}_{A\beta} = \frac{\tilde{\rho}_{A\beta}}{\langle \rho_\beta\rangle^\beta + \tilde{\rho}_\beta} \tag{B.33}$$

If we assume that $\langle \rho_\beta\rangle^\beta \gg \tilde{\rho}_\beta$, then we can express the average and deviation of the mass fraction as

$$\langle \omega_{A\beta}\rangle^\beta = \frac{\langle \rho_{A\beta}\rangle^\beta}{\langle \rho_\beta\rangle^\beta} \quad \text{and} \quad \tilde{\omega}_{A\beta} = \frac{\tilde{\rho}_{A\beta}}{\langle \rho_\beta\rangle^\beta} \tag{B.34}$$

Employing the expansion $\rho_\beta = \langle \rho_\beta\rangle^\beta + \tilde{\rho}_\beta$, and assuming $\rho_\beta \gg \tilde{\rho}_\beta$, yields the estimate $\rho_\beta = \langle \rho_\beta\rangle^\beta$ and expanding the mass fraction terms in (B.29a) and (B.31)

$$\nabla \cdot \left(\tilde{\mathbf{v}}_\beta \langle \rho_{A\beta}\rangle^\beta\right) + \nabla \cdot (\mathbf{v}_\beta \tilde{\rho}_{A\beta}) = \nabla \cdot \mathscr{D}_{AB} \left(\nabla \tilde{\rho}_{A\beta} - \frac{\tilde{\rho}_{A\beta}}{\langle \rho_\beta\rangle^\beta} \nabla \langle \rho_\beta\rangle^\beta\right) + a_v \varepsilon_\beta^{-1} \frac{k}{\left(1 + K\langle \rho_{A\beta}\rangle^\beta\right)^2} \frac{\partial \langle \rho_{A\beta}\rangle^\beta}{\partial t} \tag{B.35a}$$

$$\text{B.C.1} \quad -\mathbf{n}_{\beta\sigma} \mathscr{D}_{AB} \cdot \left(\nabla \tilde{\rho}_{A\beta} - \frac{\tilde{\rho}_{A\beta}}{\langle \rho_\beta\rangle^\beta} \nabla \langle \rho_\beta\rangle^\beta\right) = \mathbf{n}_{\beta\sigma} \cdot \mathscr{D}_{AB} \left(\nabla \langle \rho_{A\beta}\rangle^\beta - \frac{\langle \rho_{A\beta}\rangle^\beta}{\langle \rho_\beta\rangle^\beta} \nabla \langle \rho_\beta\rangle^\beta\right) + \frac{k\left(1 - \left(\frac{\langle \rho_{A\beta}\rangle^\beta}{\langle \rho_\beta\rangle^\beta}\right)\right)}{\left(1 + K\langle \rho_{A\beta}\rangle^\beta\right)^2} \frac{\partial \langle \rho_{A\beta}\rangle^\beta}{\partial t} \quad \text{at } A_{\beta\sigma} \tag{B.35b}$$

The terms containing $(\tilde{\rho}_{A\beta}/\langle \rho_\beta\rangle^\beta)\nabla \langle \rho_\beta\rangle^{\beta-1}$ can be eliminated based on estimates

$$\nabla \tilde{\rho}_{A\beta} = \mathrm{O}\left(\frac{\tilde{\rho}_{A\beta}}{\ell_\beta}\right) \tag{B.36}$$

$$(\tilde{\rho}_{A\beta}/\langle \rho_\beta\rangle^\beta)\nabla \langle \rho_\beta\rangle^{\beta-1} = \mathrm{O}\left(\frac{\langle \rho_\beta\rangle^\beta \tilde{\rho}_{A\beta}}{L \Delta \rho_\beta}\right) \tag{B.37}$$

and subject to

$$\text{Constraint:} \quad \frac{\ell_\beta}{L} \frac{\Delta \langle \rho_\beta\rangle^\beta}{\langle \rho_\beta\rangle^\beta} \ll 1 \tag{B.38}$$

For a spatially periodic porous media (see [9, Section 3.3.1]) the full simplified closure problem is

$$\nabla \cdot \left(\tilde{\mathbf{v}}_\beta \langle \rho_{A\beta} \rangle^\beta\right) + \nabla \cdot (\mathbf{v}_\beta \tilde{\rho}_{A\beta}) = \nabla \cdot D_{AB} \nabla \tilde{\rho}_{A\beta} + a_v \varepsilon_\beta^{-1} \frac{k}{\left(1 + K \langle \rho_{A\beta} \rangle^\beta\right)^2} \frac{\partial \langle \rho_{A\beta} \rangle^\beta}{\partial t} \tag{B.39a}$$

$$\text{B.C.1} \quad -\mathbf{n}_{\beta\sigma} D_{AB} \cdot \nabla \tilde{\rho}_{A\beta} = \mathbf{n}_{\beta\sigma} \cdot D_{AB} \langle \rho_\beta \rangle^\beta \nabla \left(\frac{\langle \rho_{A\beta} \rangle^\beta}{\langle \rho_\beta \rangle^\beta} \right) + \frac{k\left(1 - \left(\frac{\langle \rho_{A\beta} \rangle^\beta}{\langle \rho_\beta \rangle^\beta}\right)\right)}{\left(1 + K \langle \rho_{A\beta} \rangle^\beta\right)^2} \frac{\partial \langle \rho_{A\beta} \rangle^\beta}{\partial t} \quad \text{at } A_{\beta\sigma} \tag{B.39b}$$

$$\text{Periodicity:} \quad \tilde{\rho}_{A\beta}(\mathbf{r} + \ell_i) = \tilde{\rho}_{A\beta}(\mathbf{r}), \quad i = 1, 2, 3 \tag{B.39c}$$

Appendix C. Closure equations and estimates for closure variables

C.1. Development of coupled boundary value problems

The closure equations for mass and momentum can be restated as

Mass:

$$\underbrace{\nabla \cdot \left(\langle \rho_{A\beta} \rangle^\beta \tilde{\mathbf{v}}_\beta\right)}_{\text{Coupling and source}} + \nabla \cdot (\mathbf{v}_\beta \tilde{\rho}_{A\beta}) = \nabla \cdot D_{AB} \nabla \tilde{\rho}_{A\beta} + a_v \varepsilon_\beta^{-1} \underbrace{\frac{k}{\left(1 + K \langle \rho_{A\beta} \rangle^\beta\right)^2} \frac{\partial \langle \rho_{A\beta} \rangle^\beta}{\partial t}}_{\text{Source}} \tag{C.1a}$$

$$\text{B.C.1} \quad -\mathbf{n}_{\beta\sigma} \cdot D_{AB} \nabla \tilde{\rho}_{A\beta} = \underbrace{\mathbf{n}_{\beta\sigma} \cdot D_{AB} \langle \rho_\beta \rangle^\beta \nabla \left(\frac{\langle \rho_{A\beta} \rangle^\beta}{\langle \rho_\beta \rangle^\beta} \right)}_{\text{Source}} + \underbrace{\frac{k\left(1 - \frac{\langle \rho_{A\beta} \rangle^\beta}{\langle \rho_\beta \rangle^\beta}\right)}{\left(1 + K \langle \rho_{A\beta} \rangle^\beta\right)^2} \frac{\partial \langle \rho_{A\beta} \rangle^\beta}{\partial t}}_{\text{Source}} \quad \text{at } A_{\beta\sigma} \tag{C.1b}$$

$$\text{Periodicity:} \quad \tilde{\rho}_{A\beta}(\mathbf{r} + \ell_i) = \tilde{\rho}_{A\beta}(\mathbf{r}), \quad i = 1, 2, 3 \tag{C.1c}$$

Momentum:

$$0 = -\nabla \tilde{p}_\beta + \mu_\beta \nabla^2 \tilde{\mathbf{v}}_\beta - \varepsilon_\beta^{-1} \frac{1}{V} \int_{A_{\beta\sigma}} \mathbf{n}_{\beta\sigma} \cdot [-\mathbf{I} \tilde{p}_\beta + \mu_\beta \nabla \tilde{\mathbf{v}}_\beta] \, dA \tag{C.2a}$$

$$\nabla \cdot \tilde{\mathbf{v}}_\beta = 0 \tag{C.2b}$$

$$\text{B.C.1} \quad \tilde{\mathbf{v}}_\beta \cdot \mathbf{t}_{\beta\sigma} = \underbrace{\mathbf{z}_{\beta\sigma} \cdot \nabla \left(\frac{\langle \rho_{A\beta} \rangle^\beta}{\langle \rho_\beta \rangle^\beta} \right)}_{\text{Source}} + \underbrace{\mathbf{z}_{\beta\sigma} \cdot \nabla \left(\frac{\tilde{\rho}_{A\beta}}{\langle \rho_\beta \rangle^\beta} \right)}_{\text{Coupling}} - \underbrace{\langle \mathbf{v}_\beta \rangle^\beta \cdot \mathbf{t}_{\beta\sigma}}_{\text{Source}} \quad \text{at } A_{\beta\sigma} \tag{C.2c}$$

$$\text{B.C.2} \quad \tilde{\mathbf{v}}_\beta \cdot \mathbf{n}_{\beta\sigma} = -\underbrace{\langle \mathbf{v}_\beta \rangle^\beta \cdot \mathbf{n}_{\beta\sigma}}_{\text{Source}} \quad \text{at } A_{\beta\sigma} \tag{C.2d}$$

$$\text{Periodicity:} \quad \tilde{p}_\beta(\mathbf{r} + \ell_i) = \tilde{p}_\beta(\mathbf{r}), \quad \tilde{\mathbf{v}}_\beta(\mathbf{r} + \ell_i) = \tilde{\mathbf{v}}_\beta(\mathbf{r}), \quad i = 1, 2, 3 \tag{C.2e}$$

$$\text{Average:} \quad \langle \tilde{\mathbf{v}}_\beta \rangle^\beta = 0 \tag{C.2f}$$

where we have utilized the definition

$$\mathbf{z}_{\beta\sigma} = \frac{D_{AB} \mathbf{t}_{\beta\sigma}}{\left(\frac{\langle \rho_{A\beta} \rangle^\beta}{\langle \rho_\beta \rangle^\beta} \right) + \alpha}$$

Employing the method of superposition, we can develop boundary value problems for our closure variables (Eqs. (32)–(34)) based on Eqs. (C.1) and (C.2).

Velocity and pressure closure:

Problem I

$$0 = -\nabla \mathbf{b}_\beta + \nabla^2 \mathbf{B}_\beta - \varepsilon_\beta^{-1} \frac{1}{V} \int_{A_{\beta\sigma}} \mathbf{n}_{\beta\sigma} \cdot [-\mathbf{I} \mathbf{b}_\beta + \nabla \mathbf{B}_\beta] \, dA \tag{C.3a}$$

$$\nabla \cdot \mathbf{B}_\beta = 0 \tag{C.3b}$$

$$\text{B.C.} \quad \mathbf{B}_\beta \cdot \mathbf{t}_{\beta\sigma} = \mathbf{z}_{\beta\sigma} \cdot \nabla \left(\frac{\mathbf{d}_\beta}{\langle \rho_\beta \rangle^\beta} \right) - \mathbf{I} \cdot \mathbf{t}_{\beta\sigma} \quad \text{at } A_{\beta\sigma} \tag{C.3c}$$

$$\text{B.C.} \quad \mathbf{B}_\beta \cdot \mathbf{n}_{\beta\sigma} = -\mathbf{I} \cdot \mathbf{n}_{\beta\sigma} \quad \text{at } A_{\beta\sigma} \tag{C.3d}$$

$$\text{Periodicity:} \quad \mathbf{b}_\beta(\mathbf{r} + \ell_i) = \mathbf{b}_\beta(\mathbf{r}), \quad \mathbf{B}_\beta(\mathbf{r} + \ell_i) = \mathbf{B}_\beta(\mathbf{r}), \quad i = 1, 2, 3 \tag{C.3e}$$

$$\text{Average:} \quad \langle \mathbf{B}_\beta \rangle^\beta = 0 \tag{C.3f}$$

Problem II

$$0 = -\nabla \mathbf{c}_\beta + \nabla^2 \mathbf{C}_\beta - \varepsilon_\beta^{-1} \frac{1}{V} \int_{A_{\beta\sigma}} \mathbf{n}_{\beta\sigma} \cdot [-\mathbf{I}\mathbf{c}_\beta + \nabla \mathbf{C}_\beta] \, \mathrm{d}A \tag{C.4a}$$

$$\nabla \cdot \mathbf{C}_\beta = 0 \tag{C.4b}$$

$$\text{B.C.} \quad \mathbf{C}_\beta \cdot \mathbf{t}_{\beta\sigma} = \mathbf{z}_{\beta\sigma} \cdot \left(\mathbf{I} + \nabla \left(\frac{\mathbf{e}_\beta}{\langle \rho_\beta \rangle^\beta} \right) \right) \quad \text{at } A_{\beta\sigma} \tag{C.4c}$$

$$\text{B.C.} \quad \mathbf{C}_\beta \cdot \mathbf{n}_{\beta\sigma} = 0 \quad \text{at } A_{\beta\sigma} \tag{C.4d}$$

$$\text{Periodicity:} \quad \mathbf{c}_\beta(\mathbf{r} + \ell_i) = \mathbf{c}_\beta(\mathbf{r}), \quad \mathbf{C}_\beta(\mathbf{r} + \ell_i) = \mathbf{C}_\beta(\mathbf{r}), \quad i = 1, 2, 3 \tag{C.4e}$$

$$\text{Average:} \quad \langle \mathbf{C}_\beta \rangle^\beta = 0 \tag{C.4f}$$

Problem III

$$0 = -\nabla j_\beta + \nabla^2 \mathbf{h}_\beta - \varepsilon_\beta^{-1} \frac{1}{V} \int_{A_{\beta\sigma}} \mathbf{n}_{\beta\sigma} \cdot [-\ell j_\beta + \nabla \mathbf{h}_\beta] \, \mathrm{d}A \tag{C.5a}$$

$$\nabla \cdot \mathbf{h}_\beta = 0 \tag{C.5b}$$

$$\text{B.C.} \quad \mathbf{h}_\beta \cdot \mathbf{t}_{\beta\sigma} = \mathbf{z}_{\beta\sigma} \cdot \nabla \left(\frac{f_\beta}{\langle \rho_\beta \rangle^\beta} \right) \quad \text{at } A_{\beta\sigma} \tag{C.5c}$$

$$\text{B.C.} \quad \mathbf{h}_\beta \cdot \mathbf{n}_{\beta\sigma} = 0 \quad \text{at } A_{\beta\sigma} \tag{C.5d}$$

$$\text{Periodicity:} \quad j_\beta(\mathbf{r} + \ell_i) = j_\beta(\mathbf{r}), \quad \mathbf{h}_\beta(\mathbf{r} + \ell_i) = \mathbf{h}_\beta(\mathbf{r}), \quad i = 1, 2, 3 \tag{C.5e}$$

$$\text{Average:} \quad \langle \mathbf{h}_\beta \rangle^\beta = 0 \tag{C.5f}$$

Species density closure:

Problem I

$$\langle \mathbf{v}_\beta \rangle^\beta \cdot \nabla \cdot (\mathbf{v}_\beta \mathbf{d}_\beta) + \nabla \cdot \left(\mathbf{B}_\beta \cdot \langle \mathbf{v}_\beta \rangle^\beta \langle \rho_{A\beta} \rangle^\beta \right) = \nabla \cdot \left(D_{AB} \langle \mathbf{v}_\beta \rangle^\beta \cdot \nabla \mathbf{d}_\beta \right) \tag{C.6a}$$

$$\text{B.C.} \quad \mathbf{n}_{\beta\sigma} \cdot \nabla \mathbf{d}_\beta = 0 \quad \text{at } A_{\beta\sigma} \tag{C.6b}$$

$$\text{Periodicity:} \quad \mathbf{d}_\beta(\mathbf{r} + \ell_i) = \mathbf{d}_\beta(\mathbf{r}), \quad i = 1, 2, 3 \tag{C.6c}$$

We have neglected variations of the volume average velocity in the first term on the left-hand side and the term on the right-hand side in Eq. (C.6a). These variations cannot be neglected in the second term on the left-hand side because of the presence of the volume average species density within the gradient along with Eq. (C.3b) which states $\nabla \cdot \mathbf{B}_\beta = 0$. In other words, the divergence of the average velocity would not be a dominant term in the first term on the left-hand side and the term on the right-hand side of Eq. (C.6a) but it may be in the second term on the left-hand side.

Problem II

$$\nabla \cdot (\mathbf{v}_\beta \mathbf{e}_\beta) + \nabla \cdot \left[(\mathbf{C}_\beta) \langle \rho_{A\beta} \rangle^\beta \right] = \nabla \cdot (D_{AB} \nabla \mathbf{e}_\beta) \tag{C.7a}$$

$$\text{B.C.} \quad -\mathbf{n}_{\beta\sigma} \cdot \nabla \mathbf{e}_\beta = \mathbf{n}_{\beta\sigma} \cdot \mathbf{I} \langle \rho_\beta \rangle^\beta \quad \text{at } A_{\beta\sigma} \tag{C.7b}$$

$$\text{Periodicity:} \quad \mathbf{e}_\beta(\mathbf{r} + \ell_i) = \mathbf{e}_\beta(\mathbf{r}), \quad i = 1, 2, 3 \tag{C.7c}$$

We have ignored variations in the gradient of the species mass fraction in all terms in Eq. (C.7a).

Problem III

$$\nabla \cdot (\mathbf{v}_\beta f_\beta) + \left(\frac{k}{\left(1 + K \langle \rho_{A\beta} \rangle^\beta\right)^2} \frac{\partial \langle \rho_{A\beta} \rangle^\beta}{\partial t} \right)^{-1} \nabla \cdot \left[\left(\mathbf{h}_\beta \frac{k}{\left(1 + K \langle \rho_{A\beta} \rangle^\beta\right)^2} \frac{\partial \langle \rho_{A\beta} \rangle^\beta}{\partial t} \right) \langle \rho_{A\beta} \rangle^\beta \right] = \nabla \cdot (D_{AB} \nabla f_\beta) + a_v \varepsilon_\beta^{-1} \tag{C.8a}$$

$$\text{B.C.} \quad -\mathbf{n}_{\beta\sigma} \cdot \nabla f_\beta = \frac{\left(1 - \frac{\langle \rho_{A\beta} \rangle^\beta}{\langle \rho_\beta \rangle^\beta}\right)}{D_{AB}} \quad \text{at } A_{\beta\sigma} \tag{C.8b}$$

$$\text{Periodicity:} \quad f_\beta(\mathbf{r} + \ell_i) = f_\beta(\mathbf{r}), \quad i = 1, 2, 3 \tag{C.8c}$$

C.2. Estimates of the conductivity terms in the closed momentum equation

The sorptive "conductivity" term in Eq. (40) can be expanded as

$$\mathbf{k}_{\text{sorb},\beta} = \mathbf{K}_\beta \cdot \underbrace{\frac{k}{\left(1 + K \langle \rho_{A\beta} \rangle^\beta\right)^2} \left[\varepsilon_\beta^{-1} \frac{1}{V} \int_{A_{\beta\sigma}} \mathbf{n}_{\beta\sigma} \cdot [-\mathbf{I} j_\beta + \nabla \mathbf{h}_\beta] \, \mathrm{d}A \right]}_{\mathbf{m}_\beta} \tag{C.9}$$

From the closure equation (C.5a), the term in brackets can be expressed as

$$\varepsilon_\beta^{-1} \frac{1}{V} \int_{A_{\beta\sigma}} \mathbf{n}_{\beta\sigma} \cdot [-\mathbf{I} j_\beta + \nabla \mathbf{h}_\beta] \, \mathrm{d}A = -\nabla j_\beta + \nabla^2 \mathbf{h}_\beta \tag{C.10}$$

We estimate f_β from Eq. (C.8b) as

$$f_\beta = \mathrm{O}\left(\frac{\left(\frac{\langle \rho_{A\beta} \rangle^\beta}{\langle \rho_\beta \rangle^\beta} - 1 \right) \ell_\beta}{D_{AB}} \right) \tag{C.11}$$

where the divergence of f_β has been estimated as the magnitude of f_β divided by the micro-length-scale. An expression for $\mathbf{h}_\beta$ can be obtained from Eq. (C.5c). We can estimate $\mathbf{h}_\beta$ utilizing Eq. (C.11) and the definition of $\mathbf{z}_{\beta\sigma}$

$$\mathbf{h}_\beta = \mathrm{O}\left(\frac{\frac{\langle\rho_{A\beta}\rangle^\beta}{\langle\rho_\beta\rangle^\beta}-1}{\langle\rho_{A\beta}\rangle^\beta+\langle\rho_\beta\rangle^\beta\alpha}\right) \tag{C.12}$$

Utilizing this estimate in Eq. (C.10) we will arrive at

$$\varepsilon_\beta^{-1}\frac{1}{V}\int_{A_{\beta\sigma}}\mathbf{n}_{\beta\sigma}\cdot[-\mathbf{I}j_\beta+\nabla\mathbf{h}_\beta]\,\mathrm{d}A = \mathrm{O}\left(\frac{1}{\ell_\beta^2}\left(\frac{\frac{\langle\rho_{A\beta}\rangle^\beta}{\langle\rho_\beta\rangle^\beta}-1}{\langle\rho_{A\beta}\rangle^\beta+\langle\rho_\beta\rangle^\beta\alpha}\right)\right) \tag{C.13}$$

where we should note that Eq. (C.13) relies on the assumption that $j_\beta \leqslant \mathrm{O}(\nabla\mathbf{h}_\beta)$. If the estimate represented by Eq. (C.13) is employed in Eq. (C.9) along with the idea that $\mathbf{K}_\beta = \mathrm{O}(\ell_\beta^2)$, we obtain the final estimate

$$\mathbf{k}_{\mathrm{sorb},\beta} = \mathrm{O}\left[\left(\frac{k}{\left(1+K\langle\rho_{A\beta}\rangle^\beta\right)^2}\right)\left(\frac{\langle\omega_{A\beta}\rangle^\beta-1}{\langle\rho_{A\beta}\rangle^\beta+\langle\rho_\beta\rangle^\beta\alpha}\right)\right] \tag{C.14}$$

Turning our attention to the slip velocity term the slip "conductivity" can be expanded as

$$\mathbf{K}_{\mathrm{slip},\beta} = \mathbf{K}_\beta\left[\varepsilon_\beta^{-1}\frac{1}{V}\int_{A_{\beta\sigma}}\mathbf{n}_{\beta\sigma}\cdot[-\mathbf{I}\mathbf{c}_\beta+\nabla\mathbf{C}_\beta]\,\mathrm{d}A\right] \tag{C.15}$$

From Eq. (C.7b), we obtain the estimate

$$\mathbf{e}_\beta = \mathrm{O}\left(\ell_\beta\langle\rho_\beta\rangle^\beta\right) \tag{C.16}$$

Utilizing this estimate in Eq. (C.4c) yields

$$\mathbf{C}_\beta = \mathrm{O}\left(\frac{D_{AB}}{\langle\omega_{A\beta}\rangle^\beta+\alpha}\right) \tag{C.17}$$

when combined with the closure Eq. (C.4a), we obtain

$$\varepsilon_\beta^{-1}\frac{1}{V}\int_{A_{\beta\sigma}}\mathbf{n}_{\beta\sigma}\cdot[-\mathbf{I}\mathbf{c}_\beta+\nabla\mathbf{C}_\beta]\,\mathrm{d}A = \mathrm{O}\left(\frac{1}{\ell_\beta^2}\frac{D_{AB}}{\langle\omega_{A\beta}\rangle^\beta+\alpha}\right) \tag{C.18}$$

where Eq. (C.18) assumes $\mathbf{c}_\beta \leqslant \mathrm{O}(\nabla\mathbf{C}_\beta)$. If the estimate represented by Eq. (C.18) is employed in Eq. (C.23) along with the idea that $\mathbf{K}_\beta = \mathrm{O}(\ell_\beta^2)$ we obtain the final estimate

$$\mathbf{K}_{\mathrm{slip},\beta} = \mathrm{O}\left(\frac{D_{AB}}{\langle\omega_{A\beta}\rangle^\beta+\alpha}\right) \tag{C.19}$$

which provides a macroscopic slip velocity with the same form as the micro-scale representation presented in Eq. (7c).

C.3. Estimates of the closure terms in the closed mass equation

First we will examine the time derivative term on the right-hand side. From Eq. (C.8b) we can obtain the estimate (as in Eq. (C.11))

$$f_\beta = \mathrm{O}\left(\frac{\ell_\beta\left(\langle\omega_{A\beta}\rangle^\beta-1\right)}{D_{AB}}\right) \tag{C.20}$$

Estimates of the two components of the time derivative term in Eq. (44) can be made as follows:

$$\varepsilon_\beta^{-1}\nabla\cdot\left[\frac{k}{\left(1+K\langle\rho_{A\beta}\rangle^\beta\right)^2}D_{AB}\left(\frac{1}{V}\int_{A_{\beta\sigma}}\mathbf{n}_{\beta\sigma}f_\beta\,\mathrm{d}A\right)\frac{\partial\langle\rho_{A\beta}\rangle^\beta}{\partial t}\right] = \mathrm{O}\left(\frac{k}{\left(1+K\langle\rho_{A\beta}\rangle^\beta\right)^2}\frac{\left(\langle\omega_{A\beta}\rangle^\beta-1\right)}{L}\varepsilon_\beta^{-1}\frac{\partial\langle\rho_{A\beta}\rangle^\beta}{\partial t}\right) \tag{C.21a}$$

$$\varepsilon_\beta^{-1}\nabla\cdot\left[\frac{k}{\left(1+K\langle\rho_{A\beta}\rangle^\beta\right)^2}\langle\tilde{\mathbf{v}}_\beta f_\beta\rangle\frac{\partial\langle\rho_{A\beta}\rangle^\beta}{\partial t}\right] = \mathrm{O}\left(\frac{k}{\left(1+K\langle\rho_{A\beta}\rangle^\beta\right)^2}\frac{\langle\mathbf{v}_\beta\rangle^\beta\ell_\beta\left(\langle\omega_{A\beta}\rangle^\beta-1\right)}{D_{AB}L}\varepsilon_\beta^{-1}\frac{\partial\langle\rho_{A\beta}\rangle^\beta}{\partial t}\right) \tag{C.21b}$$

In both case divergences are taken of averaged and macro-scale terms so the length scale L is utilized. The adsorption term on the left-hand side can be expressed as

$$\left(a_v\varepsilon_\beta^{-1}\frac{k}{\left(1+K\langle\rho_{A\beta}\rangle^\beta\right)^2}\right)\frac{\partial\langle\rho_{A\beta}\rangle^\beta}{\partial t} = \mathrm{O}\left(\frac{\varepsilon_\beta^{-1}}{\ell_\beta}\left(\frac{k}{\left(1+K\langle\rho_{A\beta}\rangle^\beta\right)^2}\right)\frac{\partial\langle\rho_{A\beta}\rangle^\beta}{\partial t}\right) \tag{C.22}$$

On the basis of these estimates, we can eliminate the time derivative variable on the right-hand side of Eq. (44) relative to the left-hand side subject to

$$\text{Constraint:}\quad \left\{ \frac{\ell_\beta}{L}\left(\langle\omega_{A\beta}\rangle^\beta - 1\right), \left[\frac{\ell_\beta}{L}\left(\langle\omega_{A\beta}\rangle^\beta - 1\right) \times \left(\frac{\langle\mathbf{v}_\beta\rangle^\beta \ell_\beta}{D_{AB}}\right)\right]\right\} \ll 1 \tag{C.23}$$

The last term in Eq. (45) can be estimated based on the following arguments. First, expanding the source term in (C.6a) and utilizing Eq. (C.3b) yields

$$\nabla\cdot\left(\mathbf{B}_\beta\cdot\langle\mathbf{v}_\beta\rangle^\beta\langle\rho_{A\beta}\rangle^\beta\right) = \mathbf{B}_\beta\langle\rho_{A\beta}\rangle^\beta : \nabla\langle\mathbf{v}_\beta\rangle^\beta + \mathbf{B}_\beta\cdot\langle\mathbf{v}_\beta\rangle^\beta\cdot\nabla\langle\rho_{A\beta}\rangle^\beta \tag{C.24}$$

Employing the idea that in the closure equations the volume averaged velocity changes over the small length scale, ℓ_β while the averaged species density changes over the large length scale L the following estimates can be obtained:

$$\mathbf{B}_\beta\langle\rho_{A\beta}\rangle^\beta : \nabla\langle\mathbf{v}_\beta\rangle^\beta = \mathrm{O}\left(\frac{\mathbf{B}_\beta\langle\rho_{A\beta}\rangle^\beta\langle\mathbf{v}_\beta\rangle^\beta}{\ell_\beta}\right) \tag{C.25a}$$

$$\mathbf{B}_\beta\cdot\langle\mathbf{v}_\beta\rangle^\beta\cdot\nabla\langle\rho_{A\beta}\rangle^\beta = \mathrm{O}\left(\frac{\mathbf{B}_\beta\langle\rho_{A\beta}\rangle^\beta\langle\mathbf{v}_\beta\rangle^\beta}{L}\right) \tag{C.25b}$$

In the closure problem variation of the average velocity will correlate with the micro-length-scale (i.e., for a problem posed at the pore scale the velocity will vary significantly over the diameter of the pore) while variations in the average species density will occur only over the macro-scale. Eq. (C.3d) gives us the further estimate

$$\mathbf{B}_\beta = \mathrm{O}(1) \tag{C.26}$$

Along with Eqs. (C.25a) and (C.25b) this allows us to estimate the terms in Eq. (C.6a) as

$$\mathrm{O}\left(\frac{\left(\langle\mathbf{v}_\beta\rangle^\beta\right)^2\mathbf{d}_\beta}{\ell_\beta}\right) + \mathrm{O}\left(\frac{\langle\mathbf{v}_\beta\rangle^\beta\langle\rho_{A\beta}\rangle^\beta}{\ell_\beta}\right) = \mathrm{O}\left(D_{AB}\frac{\langle\mathbf{v}_\beta\rangle^\beta\mathbf{d}_\beta}{\ell_\beta^2}\right) \tag{C.27}$$

Thus, $\mathbf{d}_\beta$ can be expressed as

$$\mathbf{d}_\beta = \mathrm{O}\left(\frac{\langle\rho_{A\beta}\rangle^\beta}{D_{AB}/\ell_\beta - \langle\mathbf{v}_\beta\rangle^\beta}\right) \tag{C.28}$$

For many cases of environmental significance in the gas-phase, $D_{AB}/\ell_\beta \gg \langle\mathbf{v}_\beta\rangle^\beta$ leading to

$$\mathbf{d}_\beta = \mathrm{O}\left(\frac{\langle\rho_{A\beta}\rangle^\beta\ell_\beta}{D_{AB}}\right) \tag{C.29}$$

This allows us to obtain the estimates

$$\langle\tilde{\mathbf{v}}_\beta\mathbf{d}_\beta\rangle = \mathrm{O}\left[\left(\frac{\langle\mathbf{v}_\beta\rangle^\beta\ell_\beta}{D_{AB}}\right)\langle\rho_{A\beta}\rangle^\beta\right] \tag{C.30a}$$

$$D_{AB}\left(\frac{1}{V}\int_{A_{\beta\sigma}}\mathbf{n}_{\beta\sigma}\mathbf{d}_\beta\,\mathrm{d}A\right) = \mathrm{O}\left(\langle\rho_{A\beta}\rangle^\beta\right) \tag{C.30b}$$

For many cases of gas flow in porous media the estimate represented by Eq. (C.30b) will dominate over that in Eq. (C.30a) subject to the constraint (presented in Eq. (47))

$$\frac{\langle\mathbf{v}_\beta\rangle^\beta\ell_\beta}{D_{AB}} \ll 1$$

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